RECOMMENDED QUALITY ASSURANCE AND QUALITY CONTROL GUIDELINES FOR THE COLLECTION OF ENVIRONMENTAL DATA IN PUGET SOUND

Prepared for

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CONTENTS

TABLE OF CONTENTS (cont.)

TABLE OF CONTENTS (cont.)

LIST OF TABLES

LIST OF ACRONYMS

AET	Apparent Effects Threshold
ANSI	American National Standards Institute
APHA	American Public Health Association
ASQC	American Society of Quality Control
BHC	Benzene Hexachloride (represents all isomers of hexachlorocyclohexane)
BCF	Bioconcentration Factor
CLP	Contract Laboratory Program
CFR	Code of Federal Regulations
CRDL	Contract Required Detection Limit
CRM	Certified Reference Material
CSL	Cleanup Screening Level
CTD	Conductivity, Temperature, Depth
CV	Coefficient of Variation
CVAA	Cold Vapor Atomic Absorption Spectroscopy
DAIS	Dredged Analysis Information System
DDD	2,2-bis(4-Chlorophenyl)-1,1-dichloroethane
DDE	2,2-bis(4-Chlorophenyl)-1,1-dichloroethylene
DDT	1,1-bis(4-Chlorophenyl)-2,2,2-trichloroethane
DFTPP	Decafluorotriphenylphosphine
DQO	Data Quality Objective
EPA	United States Environmental Protection Agency
GC-ECD	Gas Chromatography - Electron Capture Detector
GC-MS	Gas Chromatography - Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption Detection
HPAH	High Molecular Weight Polycyclic Aromatic Hydrocarbons
ICP	Inductively Coupled Argon Plasma Spectrophotometry
ICP-AES	Inductively Coupled Argon Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Argon Plasma Spectroscopy - Mass Spectrometry
IRIS	Integrated Risk Information System
LLD	Lower Limit of Detection
LPAH	Low Molecular Weight Polycyclic Aromatic Hydrocarbons
MCL	Minimum Contaminant Level

MCUL	Minimum Cleanup Level
MDL	Method Detection Limit
MSA	Method of Standard Addition
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCDD	Polychlorinated Dibenzo-*p*-dioxin
PCDF	Polychlorinated Dibenzofuran
PLOD	Project Limit of Detection
PSAMP	Puget Sound Ambient Monitoring Program
PSDDA	Puget Sound Dredged Disposal Analysis
PSEP	Puget Sound Estuary Program
PSP&G	Puget Sound Protocols and Guidelines

LIST OF ACRONYMS (continued)

PSWQA	Puget Sound Water Quality Authority
PSWQAT	Puget Sound Water Quality Action Team (formerly PSWQA)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RDL	Reporting Detection Limit
RPD	Relative Percent Difference
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SCUM1	Sediment Source Control Standards User Manual
SCUM2	Sediment Cleanup Standards User Manual
SDL	Sample Detection Limit
SEDQUAL	Sediment Quality Database
SIZ	Sediment Impact Zone
SMS	Sediment Management Standards
SQS	Sediment Quality Standards
SRM	Standard Reference Material
TCDD	2,3,7,8 Congener of Tetrachloro Dibenzo-*p*-Dioxin
TOC	Total Organic Carbon
WAC	Washington Administrative Code

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1. INTRODUCTION

The purpose of developing these guidelines is to encourage all Puget Sound environmental programs and investigations to use standard methods wherever possible. If this goal is achieved, most data collected in Puget Sound should be directly comparable and thereby capable of being shared across programs and integrated into a Sound-wide database. Data sharing is beneficial to the development and maintenance of a comprehensive water quality management program for Puget Sound.

The original Quality Assurance and Quality Control (QA/QC) guidelines have been revised to reflect current opinions and recommendations of primary investigators who provide data for the regional databases. The revision incorporates information gathered through surveys, workshops, and personal interviews conducted over the past two years. These guidelines were revised with the assistance of representatives from organizations that fund or conduct environmental studies in the Puget Sound region (Table 1).

QA/QC procedures are necessary to ensure that environmental data achieve an acceptable level of quality and that the level of quality attained is documented adequately. The goal of generating comparable data is furthered by a consistent approach to QA/QC. This chapter establishes QA/QC guidelines and requirements for sampling and analysis activities conducted in support of Puget Sound environmental programs. While the scope of this chapter focuses on QA aspects of chemical testing, many of the principles and practices described may be applied to other types of testing, including microbiological and bioassay testing.

Thorough planning is also essential, due to the inherent complexity of sampling and analysis activities. The presence of multiple programs and activities in the Puget Sound region further enhances the need for project planning. This chapter is intended to guide project planning so that resulting data are of high quality, comparable and support their intended use.

It is recognized that there is a diversity of environmental programs in Puget Sound, and alternatives exist for many of the variables being studied by these programs. This chapter uses, as examples, the sampling and analysis conducted in support of the following major environmental programs:

- National Pollutant Discharge Elimination System, Marine Monitoring Program (NPDES)
- Puget Sound Ambient Monitoring Program (PSAMP)
- Puget Sound Dredged Disposal Analysis (PSDDA)
- Washington State Department of Ecology Sediment Management Standards (SMS)

Whenever feasible, it is recommended that the guidelines in this document be used for other Puget Sound studies as well. It remains the responsibility of each project manager to become familiar with the program requirements and conduct sampling and analysis accordingly.

Table 1
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a. Attended the workshop held on January 8, 1996.
b. Workshop facilitator.
c. Provided written comments.
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2. PROJECT PLANNING

This section discusses the following topics relating to project planning:

- the purpose of preparing project planning documents,
- the requirement to plan,
- the recommended process for preparation of project planning documents, and
- establishment of data quality objectives (DQOs), an initial step in project planning.

2.1 Purpose of Project Planning

Project planning and preparation of planning documents is a vitally important part of any sampling and analysis activity that will produce environmental data. The process and documentation of project planning should be completed before samples are collected, with the purpose of ensuring that all data generated will be suitable for their intended use. This can be accomplished by focusing project participants on a systematic planning process that addresses all significant elements of sampling and analysis and by documenting the process.

Project plans will document how sampling and analysis is designed, implemented and assessed during the life cycle of the project. An appropriate level of detail should be included in the plan to define how specific QA and QC activities will be implemented.

2.2 Requirement to Plan

The requirement to plan is proposed in an EPA internal document, EPA Order 5360.1 (EPA, 1985), which establishes that all projects generating environmental data will be planned through the use of a planning document, referred to as a QAPP. Historically, contents of project plans have been established by the EPA *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* - QAMS-005/80 (EPA, 1980).

Current EPA guidance is largely based on two documents: 1) the American National Standards Institute/American Society of Quality Control (ANSI/ASQC) E4-1994 document (ANSI/ASQC, 1994), referred to as *E4*; and 2) *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations* - EPA QA/R-5 (EPA, 1994a), referred to as *R-5*. Both documents discuss recommended approaches to use and project planning document contents. Generalized elements of planning include the need to use a systematic planning process, to involve key personnel (including data users and data generators) in the process, and to specify and document the type and quality of environmental data.

Several of the major Puget Sound regulatory programs require that planning documents be prepared and approved by the agency in advance of sample collection, including sampling for NPDES permits, sampling at CERCLA, MTCA and SMS cleanup sites, and testing for dredging projects under PSDDA. Guidance documents for preparing plans under some of these programs are listed in Appendix A.

2.3 Recommended Process

The preparation of project planning documents will serve to focus the planning process and should involve all project participants. The approach to project planning and specific information that must be contained in project planning documents may be specified by the program or regulation that the data will support. In this case, the planning document must comply with program requirements. The recommended approach to project planning is to:

- identify all participants as early as possible in the project planning document preparation process,
- collaborate with key participants,
- utilize all available expertise,
- achieve consensus and approval among key participants, and
- distribute approved project planning documents prior to initiation of all work.

Collaboration in the planning stages of a project and in development of project data quality objectives, especially between the laboratory and the project manager, is strongly recommended. Benefits to the project include ensuring the laboratory is capable of meeting project analytical requirements, development of sampling and analysis procedures that are sound from a scientific and regulatory standpoint, minimization of deviations from the planning documents once they have been approved, and enhanced likelihood that project data quality objectives will be met.
Consensus and approval of key participants is documented with dated signatures from responsible parties representing each key participant. The following participants should be included in the approval process:

- project sponsor or funding agency,
- project manager and QA manager,
- agency(ies) with regulatory oversight,
- sample collection agency or firm, and
- the laboratory.

An alternative to the preparation of a formal project planning document may be considered for projects that have a time constraint, are limited in size, or do not fall under a program which requires a formal planning process. An example of a standardized planning form is presented in Appendix B. Use of the form will ensure that critical sampling and analysis elements are considered and specified before samples are collected. However, use of the form in preference to a more rigorous planning document must be approved by all participants, including regulatory agencies and data users.

2.4 Data Quality Objectives

Data quality objectives (DQOs) are qualitative and quantitative statements of the precision, bias, representativeness, completeness and comparability necessary for the data to serve project objectives (Ecology, 1991a). Additional program requirements, such as recommended detection limits, analyte lists and reporting format, may also exist and must be addressed .

2.4.1 Purpose of Establishing Data Quality Objectives

One of the critical elements of project planning is developing a complete understanding of the expected use of the data. The projected data use will place a number of expectations on the manner in which data are generated. This process is known as establishing DQOs.

To establish how data will be used, the following needs to occur:

- Determine which regulations and programs are applicable. For example, data used to support a particular program must result from the analysis of substances regulated by that program, and analytical detection limits must meet the regulatory limits of that program.
- Specify the exact decision to be made on the basis of the data. For example, comparison of concentrations in the upper 4 feet of dredged material to PSDDA Screening Level criteria to determine if the material is suitable for open-water disposal.
- Determine whether new data will be compared with historic data. When compared with historic data, a decision may be made as to whether new data indicate a change from previous conditions. Refer to *A Project Manager's Guide to Requesting and Evaluating Chemical Analyses* [Puget Sound Estuary Program (PSEP), 1991] for further discussion.
- Evaluate whether data may potentially come under legal scrutiny.

2.4.2 Program Requirements

The development of various Puget Sound programs has placed a variety of additional expectations on sampling and analysis. These may include program-specific requirements to ensure the data have an acceptable degree of statistical power, established lists of chemical criteria the data will be evaluated against, and detection limit recommendations or requirements. Several programs have well-developed requirements for a variety of data generation elements. Program requirements may also include methods for sample collection, preservation and analysis, QC, data validation and deliverables. Appendix A contains lists of project planning reference documents for some of these programs; Appendix C contains additional program specific information, organized by program.

2.4.2.1 Analyte Lists

While differing in scope and application, many Puget Sound programs have established lists of chemical criteria that are routinely used by the agencies to regulate dredging, source control and cleanup of contaminated sediments. In addition, other chemicals without promulgated criteria may be target analytes for specific projects.

2.4.2.2 Detection Limits

Some programs may require or recommend detection limits for selected analytes, or require that detection limits be lower than concentrations of human health and environmental concern. It is imperative that planning documents be designed to generate data that will meet levels of concern in these regulatory programs. Deviations from program requirements generally require advance approval from the regulatory agency, and if not approved in advance, may result in rejection of the data. Laboratories should strive to meet detection limit requirements for all undetected analytes. In those cases where high concentrations of some analytes require analysis of a diluted sample and the dilution results in non-detects for other analytes, analysis of the sample at several different dilutions may be required to meet program detection limits as fully as practical.

The selected analytical methods must produce data that represent the correct form or species of chemical as well as being capable of detecting the substance at a level at least as low as the regulatory limit. In addition, a program may have regulatory limits expressed in a unique format or unit. For example, program requirements may include data reported either on a dry-weight basis or

in units normalized to total organic carbon (TOC). These requirements should be considered during the planning process.

After establishing expected data uses and program requirements, DQOs should be developed. An overview of DQO elements follows.

2.4.3 Precision and Bias

Precision (Ecology, 1991a; EPA, 1992) is an indication of the agreement among results of replicate measurements without the assumption of knowledge of the true value, or, a measure of the scatter of data due to random error. Precision is estimated by means of replicate analyses. Results for the replicate samples must be at or above the detection limit. If they are not, precision can be evaluated by analyzing replicates of check standards or matrix spikes which are above the detection limit. The best measure of precision is the relative standard deviation (RSD) or coefficient of variation (CV):

$$RSD=CV=100s_x/\bar{x}$$

where $\bar{x}$ is the arithmetic mean of the x_i measurements and s_x is the standard deviation. The standard deviation can be calculated as follows:

$$S_x=\sqrt{\frac{1}{n-1}\left[\sum_{i=1}^{n}(x_i-\bar{x})^2\right]}$$

where n is the number of measurements.

The relative percent difference (RPD) is typically used when only two samples are available, and is calculated as follows:

$$RPD=100\frac{|x_1-x_2|}{(x_1+x_2)/2}$$

Bias is described as the deviation due to a common systematic error, i.e., a consistent tendency for results to be either greater or smaller than the true value. Bias is a measure of the difference between an analytical result and the true value of an analyte. Sources of bias (Ecology, 1991a) include calibration error, matrix interference, inability to measure all forms of the analyte, analyte contamination and physical or chemical instability of samples.

Analytical bias is evaluated on the basis of quality control samples such as check standards, method blanks and matrix spikes. Blanks can be useful indicators of bias due to contamination. Deviation due to matrix effects is assessed by comparing a measured value to an accepted reference value in a sample of known concentration (such as a standard reference material) or by determining the percent recovery of a known amount of analyte spiked into a sample (matrix spike). Bias due to matrix effects based on a matrix spike is calculated as:

$$\text{Bias} = (X_S - X_U) - K,$$

where X_S is the measured value for the spiked sample, X_U is the measured value for the unspiked sample and K is the known (calculated) spike amount.

The percent recovery (%*R*) for check standard or matrix spikes is given by:

$$\%R=100/(R_s/R_t)$$

where R_s is the result for the check standard or the difference between the results for the spiked and the unspiked samples and R_t is the known value for the check standard or the amount of the analyte added to the matrix spike.

Accuracy is described as the closeness of agreement between an observed value and a true or accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random (precision) component and a systematic error (bias) component.

Precision and bias are performance characteristics of the method used by a particular laboratory and analyst. However, both precision and bias are also dependent on procedures followed in the field during sample collection and handling. Thus, field procedures for sample collection and handling, and equipment decontamination must be developed and followed, and analytical methods that most closely meet project objectives for precision and bias (as well as other project requirements such as attainable detection limit) must be chosen.

Collection of appropriate field QC samples is a means by which to evaluate the effect of field procedures on data quality. For example, field duplicate results will provide a means of assessing consistency of sample collection technique and resultant effects on data precision; field blank results (e.g., rinsate blanks, trip blanks, preservation blanks) provide a means of assessing contamination (bias) introduced during sample collection and/or transport. Bias introduced by field procedures is difficult to assess. Project planning that adequately addresses the need to obtain representative samples will minimize this source of bias.

Expectations of achievable precision and bias should be determined, including acceptable ranges of results of quality control samples that characterize this DQO element. Data considered imprecise, biased or of compromised usability may be qualified by the laboratory or during subsequent data assessment (see Appendix D).

2.4.4 Representativeness

The term representativeness refers to selection of sampling and analytical procedures that will produce useful data that describe the environmental conditions. Collecting representative data begins with a logical sampling design. Sampling and analysis conducted to make decisions, particularly regarding regulatory compliance, should thoroughly address representativeness. For these projects it is recommended that a statistical sampling design be considered during the planning process.

Representativeness may also be affected by sample treatment that occurs after sample collection. Sample treatment includes sample splitting and removal of aliquots for analysis, and it should be conducted in a manner that is conducive to maintaining physical and chemical integrity. For example, treatment of sediment samples such as decanting overlying water or drying and grinding prior to analysis may impact data quality. Sample treatment procedures should be specified in the project planning document. Field activities also present numerous opportunities for introducing sample contamination, and other sources of random or systematic error.

2.4.5 Completeness

Completeness is a measure of the number of useable data points with respect to the number of data points specified in project planning documents. A common requirement is 95 percent completeness .

2.4.6 Data Comparability

Comparability is, in general, a qualitative concept that describes the confidence with which data may be compared to other data. Data can only be compared to other data which reflect the same measure and have been derived by methods with similar biases. Sampling and analysis should be planned in a manner that at a minimum produces data that are sufficiently comparable to other data produced for the same Puget Sound program. Ideally, data should be comparable to data collected for other Puget Sound environmental programs as well. There may be instances when it is critical that data be comparable to a particular data set. In these instances, sampling and analysis activities must be planned to accommodate this critical data comparison The goal of data comparability between programs is also important because there may be instances where data are originally collected for a specific purpose and later used for another purpose.

Elements of sampling and analysis that significantly affect data comparability include sample collection technique, analytical method and associated quality control requirements, and subsequent data handling techniques. If project data will be compared to historic and/or subsequent data, historic data should be closely examined to determine whether the target analyte list and detection limits are the same as currently required. If detection limits are not comparable, determine to what extent data can be compared. Determine how historic data were generated and whether these activities could be repeated to the extent necessary for comparability with data collected under current program requirements. If differing or modified methodologies are to be used, note this in the planning documents and discuss implications.

2.5 Contents of Project Plans

This section provides an overview of elements to consider and include in project planning documents. Several of the major Puget Sound programs have specific requirements for project planning documents (e.g., PSDDA, SMS; see Appendix A for list of reference documents to consult). Before beginning to prepare a project planning document, program-specific and/or regulatory requirements should be clarified with key participants from the appropriate regulatory agency. The following sections discuss recommended project planning elements to consider when a project does not have program-specific or regulatory planning requirements.

2.5.1 Title and Approval Sheet

The title and approval sheet should contain: the project title; the organization conducting the project; any grant or contract numbers; and dated approval signatures of the Project Manager, QA Manager, regulatory agency contact person, laboratory and others as needed.

2.5.2 Table of Contents and Distribution List

List the sections, figures, tables, references and appendices in the Table of Contents. The distribution list should include individuals (with their organizations) who will receive copies of the approved planning document and subsequent revisions. This includes managers responsible for implementing the plan, QA managers, the regulatory agency contact person and representatives of other key participant groups.

2.5.3 Background Information

Include sufficient background information to provide historical perspective for the particular project. Note historical sources of contamination and assessment of completeness of available records. Note historical data may no longer be representative of site conditions or may not meet current data quality requirements (Ecology, 1991b). Cite previous studies and available data.

2.5.4 Problem Statement

State the specific problem to be solved or decision to be made. Include a discussion of the regulatory framework.

2.5.5 Site Description

The site description should include maps or drawings showing key features of the site and proposed sampling locations, as well as descriptions of any unique difficulties presented by the site. The site description should be sufficiently detailed to verify that the sampling approach and techniques detailed in the planning document will generate representative data.

2.5.6 Project Description

Provide a description of the work to be performed and a schedule for implementation. This discussion should give an overall picture of how the project will resolve the problem defined by the problem statement. Describe in general terms, as needed, the types of measurements that will be made; applicable technical, regulatory or program-specific quality standards, criteria or objectives; special personnel and equipment requirements; assessment tools needed (program technical reviews, peer reviews, surveillances, technical audits); a schedule for the work to be performed; and required project and quality records, including the types of reports needed.

2.5.7 Project Objectives

Specify the overall objectives of the project in the context of program-specific regulatory requirements. Describe how the data will be used to support project objectives.

2.5.8 Data Quality Objectives

Include a statement of project quality objectives and measurement performance criteria. Use of the DQO process will provide quality objectives based on the expected use of the data described in the project description and the user's determination of tolerable error in the results. Consider and discuss the DQO elements of precision and bias, representativeness, completeness, and data comparability, described in Section 2.4, and their relevance to applicable program requirements.

2.5.9 Project Organization

Discuss key individuals and specify their responsibilities. At least one individual from each key participant group must be identified. Include phone numbers.

2.5.10 Experimental Design

Describe the experimental or data collection design for the project. Discuss the types and numbers of samples to be collected, the design of the sampling network, sampling locations and frequencies, sample matrices, measurement parameters of interest, relevant or required detection limits and the rationale for the design. If field screening techniques will be used to select samples for laboratory analysis, describe the criteria for sample selection. Describe how the intended sampling design will address representativeness. Discuss how the temporal and spatial distribution of sampling points will generate data that answer critical project questions.

2.5.11 Sample Collection

Specify in detail the procedures for collecting samples. Identify sampling methods, decontamination procedures, equipment and materials. Describe documentation procedures for sample collection activities. A more detailed discussion of sample collection issues to consider is presented in Section 3.

2.5.12 Analytical Methods

List parameters of interest, required detection limits and regulatory limits or other evaluation criteria for each parameter. In consultation with the laboratory, select analytical methods to meet project requirements. Discuss any expected difficulties based on the selected methods and project DQOs, such as ability to attain required detection limits for all sample matrices. Note instances where selected methods may not perform sufficiently and discuss alternatives and implications.

If modifications to reference methods are needed to meet specific performance requirements such as very low detection limits, describe the modifications and the process to be used for validating the modified method. The development of a customized analytical approach may affect data comparability; note potential effects and discuss in the data comparability section of the planning document. A more detailed discussion of issues to be considered when selecting analytical methods is presented in Section 4.

2.5.13 Quality Control Procedures

Identify QC procedures needed for both sampling and analysis. List required field QC samples, associated acceptance criteria and corrective action to be taken when field QC criteria are not met (e.g., if a sample is improperly preserved or collected in the wrong container). Identify required laboratory QC checks, such as matrix spikes, duplicates, blanks, laboratory control samples, surrogates or second column confirmation. State the frequency of analysis of each type of QC check, required control limits and corrective action required when control limits (or action limits) are exceeded or other QC criteria are not met (e.g., analyte holding times are exceeded). Describe procedures to be used to calculate precision and bias. If data are to be qualified, list the QC samples necessary for data qualification and the qualifiers that will be used. A more detailed discussion of analytical quality control is presented in Section 5.

2.5.14 Data Review, Validation and Assessment

Describe the process to be used for reviewing, validating and assessing data. Discuss the data review criteria, describe how criteria will be applied objectively and consistently, and discuss how issues will be resolved. If data are to be independently validated, specify the data qualification system to be used. Reference applicable guidelines and guidance documents, and specify how qualifiers will be assigned. Discuss how results and limitations on the use of the data will be reported to participants with decision-making authority. A more detailed discussion of data validation procedures is presented in Section 7.

Specify records which should be retained and who will maintain them. For example, records associated with projects performed in conformance with the Sediment Management Standards are to be maintained for a minimum of 10 years, in accordance with Washington Administrative Code (WAC) Chapter 173-204-610. Should a file purge be a part of the project, specify the contents, generator and recipient of the file purge.

Activities for assessing effectiveness of project implementation and associated QA/QC should be addressed, with the purpose of ensuring the project plan was implemented as prescribed. Identify the number, frequency and type of assessment activities needed for the project. Assessments may

include peer reviews, surveillance of field activities and internal or external audits of data quality. Discuss the information expected to be gained and success criteria. List the approximate schedule of activities. Identify who will perform the assessments and how results will be reported.

Describe the format (electronic and hard copy) that will be used to report results. Program-specific reporting guidance is available for SMS, PSDDA, and NPDES projects; Appendix A lists some of the available guidance documents. Identify the frequency and distribution of reports, who will prepare reports and who will receive copies.

3. SAMPLE COLLECTION

The primary goal of any sampling effort is to deliver samples to the analytical laboratory that are as representative as possible of the material from which they were collected. Field procedures impact data quality, and therefore should be planned to encourage consistency in approach and attention to factors which can affect the data. The various Puget Sound programs specify criteria that will enhance sample representativeness and aid in evaluating the quality of the resulting analytical data. These criteria include sample containers, sample size, sample preservation, equipment decontamination procedures, sample storage conditions and sample holding times. These criteria should be addressed in project planning documents, and they should be selected so that project DQOs will be met and the requirements for the Puget Sound program under which the project is carried out will be satisfied.

3.1 Itemized Sample List

An itemized sample list comprised of a summary of all locations, samples, parameters and identification of field QC samples should be prepared prior to sample collection. Determine in advance what types of field QC samples will be collected, which samples will be composited and approximate dates of collection. Each sample should be assigned a unique sample identification number which will not reveal information about the sample. This will help keep sample analyses "blind" when required. A description of the system to be used for sample identification should appear in the project planning document.

3.2 Sample Handling

Sample handling and treatment, from sample collection to delivery to the laboratory and subsequent analysis, can have a major impact on data quality. Sample containers, preservation and storage practices must be appropriate for the parameter and the program.

Sample integrity may be affected by the decontamination procedures used to prepare sampling equipment prior to collection of samples, and in between sampling sites. The type and level of decontamination should be appropriate to the sample matrix and analytes of interest. For example, if samples are being collected from a highly contaminated location for analysis of organic constituents, it may be appropriate to use a final solvent rinse to clean sampling utensils. Field procedures should incorporate prior knowledge of site conditions; e.g., samples from highly contaminated locations should be collected last.

Sample treatment after sample collection and prior to analysis can affect sample integrity. If composite samples are to be collected, procedures for composite preparation which will yield homogeneous samples and which will not effect changes in sample composition should be developed. Solid matrix samples should be homogenized with decontaminated utensils in a stainless steel bowl until the sample is of uniform color and texture. Sample material which has contacted the sides of the sampling equipment may be excluded. Large inclusions, such as twigs, leaves, shells, or rocks, should be removed prior to filling sample containers. If material is removed from the composite, this fact should be noted on the field sheet or sampling notes. If multiple subsamples are to be collected, the homogenized sample should be stirred between each one. If samples are to be collected for analysis of volatile constituents, these containers should be filled (leaving no headspace) prior to any homogenization.

Additional sample treatment that may occur prior to analysis includes filtering water samples; sediment core sectioning; sieving, drying and grinding of solid matrix samples; and decanting overlying water from sediment samples. Procedures should be developed and specified in project

planning documents for sample treatment steps to be employed.

Sample containers should be of an appropriate volume and material. If loss of target analytes into sample container headspace is possible, containers should be completely filled during collection. If sample container cleaning is critical, procedures that confirm container cleanliness should be developed.

Sample integrity may also be affected by how and when sample preservation will be performed. Samples should be preserved as soon as practicable after collection unless additional handling (e.g., sample compositing or filtration) must be done prior to preservation. Preservation may be limited to specified storage conditions or may entail addition of chemical preservatives. If chemical preservatives are added in the field, procedures should be developed to ensure the proper type and amount of chemical agent is added, the sample is well mixed with the preservative, and labels on preserved containers clearly indicate the chemical used for preservation. Chemical preservatives should be verified to be free of contamination prior to use.

Samples should be stored in a way that minimizes degradation, either by loss of constituents or by contamination in the field or laboratory. Typically, samples are kept chilled from the time of sample collection until analysis. Sample temperature should be maintained during transport and delivery to the laboratory. Longer term storage may require other techniques. It may be necessary to archive samples for future analysis, especially those collected for parameters with long holding times.

Tables 2, 3 and 4 in the *Recommended Guidelines for Sampling Marine Sediment, Water Column and Tissue in Puget Sound* (PSEP, 1997) contains minimum sample size, container, preservation technique and holding time recommendations for sediment, water and tissue samples, respectively. This chapter also contains further discussion of decontamination and sampling procedures, and guidelines for documentation of sample storage.

3.3 Chain of Custody

Chain of custody procedures should be observed when required by applicable regulations. Areas and containers which are considered controlled should be established as needed. Forms may be required to document an unbroken chain of custody process. These forms account for sample transfer between participants, delivery of samples to the laboratory, and sample splitting to generate new samples, such as the splitting of a sediment core sample. This form may also be used by the laboratory to receive and check samples. Other items which should be checked at this time include clarity and accuracy of sample identification and labeling, sample preservation and sufficiency of sample volume to conduct the requested analyses.

4. ANALYTICAL METHODS

4.1 Selection of Analytical Methods

This section provides guidance for both the selection and modification of available analytical methods. In addition, guidelines are included for the use of new methods. Reference methods are specified in the analytical chapters. Reference methods were selected for their ability to meet DQOs for at least one of the major Puget Sound Programs. The use of reference methods will enhance the comparability of data collected in the Puget Sound region.

Selection of analytical methods for a given project should begin with available reference methods, and should be guided by project DQOs or specific requirements of applicable regulations. When an analytical method is evaluated, the following critical elements must be considered:

- analyte list,
- detection limit requirements,
- method accuracy (precision and bias),
- data comparability requirements, and
- ability of the method to function under anticipated project conditions.

4.2 Method Modifications

Methods should be used as referenced or described in the analytical chapters. Analytical methods may be modified when available reference methods will not meet project DQOs or when sample analysis reveals analytical difficulty that jeopardizes the DQOs. The impact on data comparability must be addressed when modifying a method. Consider whether the modification is being made for a limited number of sampling and analysis events or whether it represents a change in analytical conditions at some point in the course of an ongoing project.

Modified methods must undergo an initial demonstration of method performance (Dux, 1990 and Garfield, 1991). The demonstration should verify that the modified method will function properly for all anticipated matrix types from the sampling site. The method should be shown to perform over the expected range of analyte concentrations at the site. This demonstration of method performance may be conducted by either comparing performance of the modified method to performance of the published method, or by conducting a study verifying performance of the modified method.

Performance of the modified method should be compared with the performance of the reference method by analyzing at least seven samples of each sample type by the method as written and at least seven samples by the method as modified. Appropriate QC samples should be included in each batch. The selected sample types should cover the range of expected matrices and target analyte concentrations. QC results from the modified method should meet performance criteria of the published method. Comparison of analytical results from the published and modified methods should include collaboration with key project participants.

In lieu of a method comparison, performance of the modified method may be verified for each matrix. Verification should be conducted by analyzing a certified reference material (CRM) or similar material if available, a method blank, a sample of each matrix type and a series of matrix spikes covering the range of expected sample matrices and analyte concentrations for the site. QC results from the modified method should meet the performance criteria of the published method.

All data should be traceable to the procedure used, and the laboratory should document the verification and use of modified methods. The data report must note the method has been modified, and the nature of the modification and potential impact on data must be indicated.

4.3 Evaluation of New Methods

New methods may be used when reference or modified reference methodology will not meet project DQOs, or when new methods or technologies become available and accepted as industry standard. Before using a new method, method performance must be verified and documented. This should be done by analyzing at least one CRM (if available) in triplicate, a method blank in duplicate, a sample of each matrix type and a series of matrix spikes covering the expected range of concentrations for the site. The laboratory should prepare a report documenting study results. A more rigorous approach to assessing method performance and data quality is discussed in the quality control section (Section 9.0) of the Environmental Monitoring Management Council's method documentation format guidance (EPA, 1993). The project manager should collaborate with key project participants prior to requesting the laboratory use a new method.

4.4 Detection and Quantification Limit

Environmental analytical chemists have not universally agreed upon terminology for defining or conventions for determining and reporting detection limits for analytical procedures. The following guidance does not attempt to resolve the debate over terms or procedures. Rather, it is intended to provide practical information that can be used as a basis for discussion between program managers and laboratories.

EPA (CFR, 1994) defines method detection limit (MDL) in Appendix B to 40 CFR Part 136 as "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the element." A copy of the complete procedure is contained in Appendix E of this document.

The intended scope and application of the EPA procedure for calculating MDL is for water and wastewater, but the approach can be adapted to solid samples with low concentrations of analytes. Step 7 of this procedure describes an operational iterative procedure involving spiking the matrix of interest with analytes of interest. Laboratories should perform this step to verify the reasonableness of the calculated MDL for a specific matrix. Program managers may require this step to demonstrate routine ability to meet program-specific sensitivity requirements, particularly for challenging sample types. Project planning documents should specify whether matrix-specific detection limits need to be calculated.

If required, matrix-specific detection limits should be demonstrated once during the life of the project for each matrix and target analyte that is not detectable at the nominal detection limit. Ongoing demonstration of ability to meet detection limits should be demonstrated by analyzing a low-level standard containing all target analytes at detection limit concentrations as a periodic check sample. The matrix-specific MDL should be adjusted for each sample to account for sample size and any dilution or concentration factors.

Detection limits may be affected by instrument sensitivity or by bias due to contamination or matrix interferences. Common laboratory practice is to adjust detection limits upward in cases where high instrument precision (i.e., low variability) results in calculated detection limits that are lower than the absolute sensitivity of the analytical instrument. In these cases, best professional judgment is used to adjust detection limits upward to reduce false positives and values below the detection limit

are not reported. In all cases, results cannot be reported for values less than the calculated MDL.

The quantification limit represents a practical and routinely achievable detection limit with relatively good certainty that any reported value is reliable (APHA, 1992). The quantification limit is always higher than the corresponding detection limit, usually by about five to ten times.

Recommended applications of detection and quantification limits follow:

- Values below the detection limit documented for a project should not be reported.
- Values between the detection and quantification limit should be reported and qualified as less than the quantification limit.
- Values above the quantification limit are useable without qualification unless QC criteria are not met or qualification is deemed appropriate during subsequent QA review.

Practical guidance for determining detection and quantitation (quantification) limits for inorganic analyses can be found in Appendix F.

5. QUALITY CONTROL SAMPLES

Quality control sample results provide information needed to evaluate method performance during analysis and to determine whether subsequent analytical results meet project DQOs. In order for QC data to fulfill both functions, there must be discussion between project managers and laboratory staff during project planning. Tables C-2, C-3, C-5, C-6, C-10 and C-11 in Appendix C list QC requirements for some of the Puget Sound programs.

5.1 Field Quality Control

Field sampling and laboratory analyses are separate but interdependent events, and QA/QC guidelines should be established and followed for both of these types of activities. Laboratory oriented quality assurance programs can only assure the quality of data generated in the laboratory, and cannot be applied to field operations, which include actual sample collection, field decontamination procedures, sample preservation and storage, sample labeling and identification, sample transport, chain of custody procedures and data management. Therefore, field activities must be governed by an appropriate set of QA guidelines in order to characterize and minimize possible sources of systematic and random errors. QA/QC procedures for field and laboratory activities should be specified in project documents.

Results of field QC samples also provide the data user with important information about data quality. Because field conditions are more difficult to control, sample collection may have a greater impact on data quality than laboratory analysis. Results of field QC samples must be evaluated in conjunction with the results of analytical QC samples in assessing data quality.

Field QC samples that may be required include:

- field blanks, container blanks, preservation blanks, rinsate blanks, trip blanks and
- field split samples and field replicates.

Any additional program-specific requirements should be listed in the planning document.

5.2 Analytical Quality Control

Whenever possible, analytical QC specified in planning documents should be consistent with analytical QC specified for the selected methods. Details of method-specific QC sample frequency, control limits and corrective actions are specified in the PSP&G analytical chapters. These chapters are useful resources for preparing planning documents. Additional program-specific QC requirements should be listed in project planning documents.

- calibration verification,
- ICP Interference check sample,
- method blank,
- detection or quantification limit check sample,
- matrix spike,
- analytical replicate or matrix spike duplicate,
- spiked method blank or check standard,
- surrogate spike compounds, and
- certified reference materials (when available).

Project or program-specific requirements for reporting QC sample results, corrective actions and data qualification should be detailed in the project planning document. During data validation, data qualifiers may be applied based on QC sample results. Tables D-1 through D-6 in Appendix D list

some program-specific data qualifiers.

6. DELIVERABLES

6.1 Laboratory Deliverables

Specific deliverable requirements must be outlined in the project planning document. Care must be taken to ensure that deliverable requirements meet project data use goals. At a minimum, the laboratory should provide a data report that includes analytical results, a tabular summary of associated QC results and control ranges, and a cover letter that references or describes the analytical procedure(s) and discusses any analytical problems. Data should be delivered from the laboratory in electronic format as well as hardcopy format.

The laboratory is responsible for providing an analytical data package which has been internally reviewed and approved for release. Data package preparation should be in accord with the laboratory's internal quality assurance procedures. All data sets should receive consistent internal review, including verification of the data summaries. Any anomalies or problems with the data set should be discussed by the laboratory.

6.2 Recommended Deliverables for Chemical Analyses

The following list contains recommended deliverables to be included in laboratory reports. Laboratory QC associated with each batch of samples should be reported.

- dates of extraction and analysis;
- tabulated sample results with units, including reporting basis (e.g., wet, dry, TOC normalized);
- summary of extraction or digestion procedure;
- detection limits, including both quantification limits and statistically derived detection limits;
- quantification of all analytes in method blanks and association of method blanks with each sample;
- tentatively identified compounds (if requested, GC-MS analyses only) and methods of quantification;
- summary of results and control limits for all associated QC analyses performed by the laboratory, such as spikes, surrogates, duplicates and CRMs;
- explanations for all data qualifications;
- explanations for all departures from the analytical protocols and discussion of possible effects on the data; and
- reference method.

6.3 Additional Reporting Requirements

Validation, an independent review of the data after the laboratory has produced this final data report, may be required. Depending on the level of data validation required (see Section 7) or if data are to be incorporated into one of the sediment quality databases, there may be additional reporting requirements placed on the laboratory. Program-specific guidelines exist describing required levels of validation. For example, the PSDDA management plan describes a QA1 data review process designed for determining suitability of sediments for unconfined, open-water disposal (Ecology, 1989). On the other hand, QA2 is defined as the process of reviewing chemical and biological data to determine if they are suitable for incorporation into regional sediment quality (e.g., SEDQUAL) databases maintained by Ecology. A complete description of QA1 and QA2 can be found in *Data Validation Guidance Manual for Selected Sediment Variables* (Ecology, 1989).

6.4 Backup Documentation

All laboratories are required to submit results that are supported by sufficient backup documentation and quality control results to enable independent QA reviewers to evaluate data quality and reconstruct final results from the raw data. Legible photocopies of original data sheets should be available from the laboratory with sufficient information to unequivocally identify the following items:

- calibration results,
- method blanks,
- samples, sample sizes and dilution factors,
- replicates and spikes, including amount spiked,
- control or reference samples,
- chromatograms,
- GC-MS tuning documentation,
- GC-MS supporting spectra,
- chain of custody and sampling records, and
- any anomalies in instrument performance or unusual instrument adjustments.

6.5 Final Deliverable to Project Manager

The project planning document should have sufficient detail to outline data delivery requirements to the final end user of the data. For example, if samples are being collected for a PSDDA project, the U.S. Army Corps of Engineers has specific requirements for data format and content. All data should be available in an electronic format. Sediment Management Standards programs require data be reported in both dry-weight and TOC-normalized units in hardcopy as well as in dry-weight electronic format (such as SEDQUAL-compatible format). Copies of Excel® spreadsheets in the required format may be obtained through the Ecology Sediment Management Unit. Other programs may have different requirements, and it is important for the laboratory to be aware of those requirements prior to analyzing samples.

If only hardcopy data are received from the laboratory, data are usually manually entered into a database or spreadsheet. Quality control measures to establish the accuracy of the final form of the electronic data are critical; i.e., the electronic version must match reviewed or validated hardcopy results. This is especially important if electronic data are produced and/or reviewed by separate procedural lines than hardcopy data. If data are manually entered, verification by a separate individual is recommended to ensure no transcription errors are made. If data are electronically transferred, a process for updating electronic data should be established to accommodate revisions made during review or validation.

7. DATA VALIDATION

7.1 Definition and Requirement for Data Validation

Data validation is defined as a process to determine if the data meet project DQOs. If the DQOs are not met, data usability is further evaluated (Ecology, 1989 and EPA, 1994b). Validation of a set of data involves several aspects: 1) reviewing the laboratory data package for transcription errors, misidentifications, or miscalculations; 2) assessing the reliability of data based on quality control sample results; and 3) verification that requirements contained in the project planning documents have been met.

Data validation can be performed with various levels of rigor. Several conventions have been established that outline data validation levels (Ecology, 1989 and EPA, 1994b). In general, validation levels define the degree to which laboratory data are scrutinized or reviewed, typically by an independent party, and are different for different programs. The data user should determine the appropriate level of validation based on the expected data use, whether the data result from routine or non-routine procedures, past

experience with validation of similar data sets from the same laboratory and program requirements. However, all data should receive a minimum level of validation, as quality control results should be evaluated prior to incorporating data into an environmental investigation. An appropriate level of data validation must be identified and detailed in the project planning document prior to sample collection.

The previous section recommended documentation that should be provided or maintained by the analytical laboratory. This documentation is necessary for independent review of the data set, and its delivery (or availability for inspection at the laboratory) should be required in the project planning document if an independent data review is to be conducted or if the data will eventually be entered into one of the regional sediment quality databases (e.g., necessitating QA2 review) .

Data validation should be performed by a qualified chemist. A reviewer performing data validation would verify the following general areas (Ecology, 1989):

- compliance with the planning document,
- proper sample collection and handling procedures,
- holding times,
- field QC results,
- instrument calibration verification,
- laboratory blank analysis,
- detection limits,
- specific instrument QC requirements,
- certified reference material results,
- laboratory replicates,
- matrix spike percent recovery results,
- surrogate percent recovery,
- calculations,
- data completeness and format, and
- data qualification.

Further data assessment is performed incorporating information generated during data validation. The reviewer performing data assessment determines if project DQOs are met by reviewing laboratory and field QC results (Ecology, 1989) and comparing them to the planning document.

7.2 Qualifiers

Data qualifiers or flags are notations based on quality control test results that are used by laboratories and data reviewers to impart qualitative information about the associated data or the systems producing data (EPA, 1994b). Data qualifiers may vary among different organizations. For this reason, a list of qualifier code definitions must be provided with the analytical data. A list of data qualifiers currently in use for one or more of the major Puget Sound programs and their definitions are presented in Appendix D. An appropriate qualification scheme must be identified and defined in the planning document. Project managers must ultimately determine whether qualified data meet their objectives for data quality and are satisfactory for their intended use.

7.3 Roles and Responsibilities

The planning document must clearly define the roles and responsibilities of all parties associated with data validation. Clear expectations must be defined for data qualifiers that the laboratory will apply and qualifiers an independent reviewer will be applying after data have been released by the laboratory. It is also important to stipulate the type and format of deliverables the laboratory must provide to ensure the appropriate level of validation can be accomplished.

8. DATA ARCHIVING AND STORAGE

Record retention and maintenance should be considered and specified during the project planning process. As discussed in Section 2, responsibilities and requirements for record keeping should be specified in the project planning documents. When archiving data, consideration should be given to any permit or regulatory requirements. In addition to any archiving procedures specified in project documents, written procedures should be established describing the following:

- printed and electronic material considered applicable records,
- record assembly and storage procedure,
- records access control,
- archive documentation,
- records retrieval process,
- duration of archived records maintenance,
- record disposal requirements, and
- procedures to protect stored records from damage, loss, or deterioration.

Records should be stored in a manner that is complete and facilitates retrieval. It is recommended that records be organized and maintained by specific project. Record keeping shall be of sufficient scope and detail to establish that project requirements were implemented and sampling and analysis specifications were achieved.

9. SUBCONTRACTING LABORATORY SERVICES

Due to the wide scope of analytical activities conducted in support of the Puget Sound programs, subcontracting samples to one or more analytical laboratories for a given project will frequently occur. The following are recommended activities for subcontracting samples.

- Procurement of a subcontractor laboratory should be carried out by qualified personnel. All documents and correspondence between the subcontractor and the hiring entity should be reviewed by qualified personnel.
- Prior to the start of work by a subcontractor, it is required that a copy of all documents specifying requirements for a given project, such as the project planning documents, be forwarded to the subcontractor. Sample analyses must be coordinated to meet program DQOs and requirements, such as running TOC analyses prior to semivolatile analyses to meet SMS program detection limit requirements.
- Upon receipt, the primary contractor of the subcontracted services should review data and other supporting documentation to ensure compliance with project requirements. For extended projects, it is recommended that review occur on an ongoing basis during the project.

Price quotations will frequently be requested from potential subcontractor laboratories prior to the completion of planning documents. These price quotations should be obtained by qualified personnel and available project information must be forwarded to potential subcontractors. This will ensure that they understand the scope of the work and can provide an appropriate price quotation. The primary contractor should have established and documented procedures to determine the capabilities and qualifications of any subcontractor. If the project requires specific lab accreditation, address the accreditation requirements of the subcontracting lab during the procurement phase.

The Washington State Department of Ecology Quality Assurance Section administers the environmental laboratory accreditation program for the analysis of (non-marine) water samples. Ecology policy requires that all results of (non-marine) water analyses reported to the agency come from an accredited laboratory. The program also includes accreditation criteria (Gries, 1991) and accredits laboratories for methods of analysis of marine sediment in support of the PSDDA program. Accreditation involves review of laboratory quality assurance procedures, periodic systems audits of the facility, and successful analysis of performance evaluation samples every six months. This requirement for PSDDA has become an expectation for many other programs.

10. GLOSSARY

Note this glossary contains terms found throughout the main body of the text and the appendices.

Accuracy - The agreement between an analytical result and the true value.

Action Limit - In Puget Sound programs, a value for results of a QC analysis that requires appropriate action be taken to correct the performance of a system or a method that is not in control. Action limits and appropriate corrective actions are specified contractually. Data obtained when a system or method is not in control may be omitted from a regional database. Note in a multianalyte method, failure to meet the calibration requirement for a small percentage of analytes should not be cause to omit the entire analysis for a sample from the database. Omission should be determined on an analyte by analyte basis. Action limits and appropriate corrective actions are specified contractually.

Analyte - That which is identified and quantified in the process of analyzing the sample.

Assessment - The evaluation process used to measure the performance or compliance of sampling and analysis activities.

Audit - A systematic and independent examination to determine whether sampling and analysis activities and related results comply with planned practices, whether these practices are implemented effectively, and whether the nature and extent of these practices are suitable for the sampling and analysis activities they support.

Batch - The number of samples that are prepared or analyzed with associated laboratory QC samples at one time. A typical batch size is 20 samples.

Bias - The systematic or persistent distortion of a measurement process which causes errors in one direction.

Blank-corrected Result - Refers to an analytical result that has been corrected (mathematically or through analytical procedures) for the contribution of the method blank. The method blank should be processed concurrently. Any correction should account mathematically for all relevant weights, volumes, dilutions and other similar sample processing elements.

Calibration - The determination of the relationship between analytical response and concentration (or mass) of the analyte.

Certified Reference Material - A reference material accompanied by, or traceable to, a certificate stating the concentration of chemicals contained in the material. The certificate is issued by an organization, public or private, that routinely certifies such material (e.g., National Research Council of Canada (NRCC), Ottawa).

Chain of Custody - An unbroken trail of accountability that ensures the physical security of samples, data and records.

Check Standard - A QC sample prepared independently of calibration standards, analyzed exactly like the samples, and used to estimate analytical precision and indicate bias due to calibration.

Coefficient of Variation - The standard deviation expressed as a percentage of the mean. Also termed

relative standard deviation or RSD.

Comparability - An indication of the confidence with which one data set can be compared to another.

Completeness - A measure of the amount of valid data obtained from sampling and analysis activities compared to the amount that was expected to be obtained.

Control Limit(s) - A value or range of values against which results of QC sample analyses are compared in order to determine whether the performance of a system or method is acceptable. Control limits are typically statistically derived. When QC results exceed established control limits, appropriate corrective action should be taken to adjust the performance of the system or method.

Corrective Action - Measures taken to remove, adjust, remedy, or counteract a malfunction or error so that a standard or required condition is subsequently met.

Data Quality Objectives - Data quality objectives are qualitative and quantitative statements that define the appropriate type and quality of data needed to support the objective of a given project.

Duplicate Analysis - Analysis performed on a second subsample in the same manner as the initial analysis, used to provide an indication of measurement precision.

Field Blank - A simulated sample (usually consisting of laboratory pure water) that is taken through all phases of sample collection and analysis. Results of field blank analyses are used to assess the positive contribution from sample collection and analysis procedures to the final result.

Guideline - A recommended practice that is non-mandatory.

Interference Check Sample - A sample run by ICP methodology to verify interelement and background correction factors.

Isotope Dilution Technique - An internal standard technique for quantification of organic compounds that uses a large number of stable isotopically labeled compounds spiked into the sample before extraction in order to provide recovery correction factors (i.e., to correct for compound loss during sample workup on a sample specific basis). The labeled compounds are analogs of the target compounds and are assumed to behave similarly. The isotopic labels typically involve replacement of hydrogen atoms with deuterium or replacement of carbon-12 atoms with carbon-13 atoms.

Matrix - The sample material in which the analytes of interest are found (e.g., water, sediment, tissue).

Matrix Spike - A QC sample created by adding known amounts of analytes of interest to an actual sample, usually prior to extraction or digestion. The matrix spike is analyzed using the normal analytical procedures. The result is then corrected for the analyte concentration determined in the unspiked sample, and expressed as a percent recovery. This provides an indication of the sample matrix effect on the recovery of target analytes.

Method - A body of procedures and techniques for performing an activity that is systematically presented in the order in which they are to be executed.

Method Blank - A QC sample intended to determine the response at zero concentration of analyte and

assess the positive contribution from sample analysis procedures to the final result. A clean matrix (generally water) known to be free of target analytes that is processed through the analytical procedure in the same manner as associated samples.

Method Detection Limit - The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing the element.

Metro - King County Water Pollution Control Division Environmental Laboratory.

Must - A requirement that is mandatory.

Normalize - Perform a data calculation in order to express results in terms of a reference parameter or characteristic.

Percent RSD - Calculated by dividing the standard deviation by the mean and multiplying by 100.

Precision - The statistical agreement among independent measurements determined from repeated applications of a method under specified conditions. Usually expressed as RPD, RSD or coefficient of variation.

Project - An organized set of activities within a program.

Qualified Data - Data to which data qualifiers have been assigned. Data qualifiers provide an indication that a performance specification in the qualified sample or an associated QC sample was not met.

Quality Assurance - An integrated system of management activities involving planning, implementation, assessment, reporting and quality improvement to ensure that a process, item or service is of the type and quality needed and expected by the customer.

Quality Assurance Project Plan - A formal planning document describing in comprehensive detail the necessary QA, QC and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

Quality Control - The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process. Quality control is an element of quality assurance. QC samples and auditing/assessment are common quality control activities.

Quantification - The process of calculating the value of an analyte in a particular sample.

Quantification Limit Check Sample - A check sample containing target analytes at concentrations at or near the quantification limit; used to verify routine method performance at the quantification limit.

Recovery - The percentage difference between two measurements, before and after spiking, relative to the concentration spiked, or the percentage difference between a measured value and a true value, as in the case of a reference material or check standard.

Reference Material - A material of known analyte composition which can be used for comparison of analytical results. The reported analyte concentrations have not been certified (see Certified Reference

Material).

Relative Percent Difference - Difference of two measurements x_1 and x_2, divided by the mean of the measurements, multiplied by 100.

Relative Standard Deviation - See Coefficient of Variation.

Replicate - One of several identical experiments, procedures, or samples.

Representativeness - A measure of the degree to which data accurately and precisely represent an environmental characteristic or condition.

Reproducibility - The ability to produce the same results for a measurement. Often measured by determining the RPD, RSD or coefficient of variation for an analysis.

Semivolatile Organic Compounds - Organic compounds with moderate or low vapor pressures that can be extracted from samples using organic solvents.

Should - Refers to a highly recommended practice. The practice may be mandatory, depending on the exact conditions of sampling and analysis.

Spike - The addition of a known amount of a substance to a sample or a blank.

Spiked Method Blank - See Check Standard.

Standard - A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of a sample. In chemical measurements, standard often describes a solution of analytes used to calibrate an instrument.

Standard Reference Material - A material with known properties produced and distributed by the U. S. National Institute of Standards and Technology (NIST).

Surrogate Spike Compound - A compound that has characteristics similar to that of a compound of interest, is not expected to be found in environmental samples and is added to a sample prior to extraction. The surrogate compound can be used to estimate the recovery of chemicals in the sample.

Target Analytes (or Target Compounds) - One or more elements or compounds which are intended to be determined by an analytical procedure (in contrast to tentatively identified compounds).

Tentatively Identified Compounds - Chemicals identified in a sample on the basis of mass spectral characteristics held in common with a reference mass spectra of a known chemical. These compounds cannot be more confidently identified unless a reliable standard of the compound is obtained and is confirmed to co-elute with the tentatively identified compound and generate similar mass spectra using the same GC-MS.

Validation - Confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Can refer to a process whereby environmental data are determined by an independent entity to be complete and final (i.e., subject to no further change), and to have their value for the intended use described by both qualitative and quantitative statements.

Volatile Organic Compounds - Organic compounds with high vapor pressures that tend to evaporate readily from a sample.

Warning Limit - In Puget Sound programs, a value for results of a QC analysis for which data returned by a laboratory are subjected to qualification before inclusion in a regional database. The principle is identical to that of an action limit, but is less stringent and serves as a warning that the system or method may not be performing normally. If necessary to meet project goals, project managers may specify warning limits as more stringent contractual limits in laboratory statements of work.

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PSEP, 1997. *Puget Sound Estuary Program, Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound*. Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, and Puget Sound Water Quality Action Team, Olympia, WA. King County Environmental Laboratory, Seattle, WA.

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EPA, 1991. *Pollutants of Concern in Puget Sound.* EPA 910/9-91-003, Prepared for U.S. Environmental Protection Agency Region 10, Office of Puget Sound, Seattle, WA. PTI Environmental Services, Bellevue, WA.

EPA, 1993. *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring.* (Commonly called the Pumpkin Book.). EPA 821-B-93-001, U.S. Environmental Protection Agency, Washington, DC.

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EPA/USACE, 1994. *Evaluation of Dredged Material Proposed for Discharge in Waters of the U. S. - Testing Manual (Draft) Inland Testing Manual.* EPA 823-B-94-002, U.S. Environmental Protection Agency, Office of Water and Department of the Army, Corps of Engineers, Washington, DC.

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PSAMP, 1990. *Puget Sound Ambient Monitoring Program - Shellfish Programs Implementation Plan.* Clive Pepe for the Puget Sound Water Quality Authority, Olympia, WA.

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U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental

Protection Agency, and Washington State Department of Natural Resources, 1988. *PSDDA Management Plan Technical Appendix (MPTA).* Exhibit I, Department of the Army, Corps of Engineers, Seattle, WA.

U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Washington State Department of Natural Resources, 1988. *Puget Sound Dredged Disposal Analysis (PSDDA) Management Plan Report, Unconfined Open Water Disposal of Dredged Material, Phase I (Central Puget Sound) (MPR, 1988).* Department of the Army, Corps of Engineers, Seattle, WA.

U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Washington State Department of Natural Resources, 1989. *Puget Sound Dredged Disposal Analysis (PSDDA) Management Plan Report, Unconfined Open Water Disposal of Dredged Material, Phase II (North and South Puget Sound) (MPR, 1989).* Department of the Army, Corps of Engineers, Seattle, WA.

U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Washington State Department of Natural Resources, 1991. - *Appendix D - Revised Modifications to Holding Times for PSDDA Chemical Analyses*. PSDDA Third Annual Review Meeting (ARM) Minutes, Tacoma WA.

U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Washington State Department of Natural Resources, 1993. *DAIS Dredged Analysis Information System Version 4.0 User's Guide.* Department of the Army, Corps of Engineers, Seattle, WA.

U.S. Army Corps of Engineers, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Washington State Department of Natural Resources, 1994. *Sampling and Analysis Plan for Sediment Characterization at Pier D.* ProTech Consulting for the Department of the Army, Corps of Engineers, Seattle, WA.

13. APPENDIX A: REFERENCE DOCUMENTS

13.1 Reference Documents Addressing Project Planning Requirements

Programs listed in Table A-1 conduct sampling and analysis in accordance with a guidance or planning document. Programs which require a project-specific planning document are identified, and applicable guidance is noted for preparing these documents. In some cases, a single planning document may be used for many sampling and analysis efforts. Note actual sampling and analysis practices agreed to and specified in the planning documents may vary on a site-specific basis from requirements listed in the reference documents. Relevant information in addition to the project planning reference document has been listed when available. Contact program managers or program contacts identified in Appendix C for information regarding the source and availability of the various documents.

13.2 Reference Documents Addressing Puget Sound Program Requirements

Table A-2 lists supporting documents cited by program managers for the major Puget Sound programs. These documents provide a starting point for understanding program requirements. Note actual sampling and analysis practices may vary from requirements listed in the referenced documents. In some cases, information in addition to the documents has been included in the table. Contact program managers or program contacts identified in Appendix C for information regarding the source and availability of these documents.

Table A-1

Project Planning Reference Documents for Some Puget Sound Programs

PROGRAM	DOCUMENT[1]
NPDES Sediments[a]	The *Sediment Sampling and Analysis Plan Appendix* to the *Sediment Source Control Standards User Manual* (*SCUM1*), published in 6/93, and the *Sediment Cleanup Standards User Manual (SCUM2*), published in 12/91, will provide guidance for project plan preparation. This appendix is currently in preparation.
NPDES Water[a]	Program requires a planning document. Program specific guidance is not identified for preparing the document.
PSAMP Fish Task	*Puget Sound Ambient Monitoring Program - Fisheries Monitoring Task Implementation Plan*, published in 6/89, is used as a planning document.
PSAMP Marine Water Task	*Marine Water Column Ambient Monitoring Wateryear 1995 Long-Term Monitoring Implementation Plan*, published in 5/95, is used as a project planning document.
PSAMP Sediment Task	*Puget Sound Ambient Monitoring Program - Marine Sediment Quality Implementation Plan*, published in 11/88 is used as a project planning document. Currently undergoing revision.
PSAMP Shellfish Task	*Puget Sound Ambient Monitoring Program - Shellfish Programs Implementation Plan*, published in 2/90, is used as a planning document.
PSDDA[a]	Refer to prototype planning document, *Sampling and Analysis Plan for Sediment Characterization at Pier D*, for guidance on how to prepare project specific planning documents.
Sediment Management Standards[a]	*Sediment Management Standards WAC Chapter 173-204* and *SCUM2* provide project planning guidance or requirements.

Notes:
1. Request information on obtaining reference documents from Program Contacts identified in Appendix C.
a. This program requires a project specific planning document.

Table A-2

Reference Documents for Some Major Puget Sound Programs

PROGRAM	TOPIC	DOCUMENT[1]
NPDES Sediments	analytical methods	*Sediment Source Control Standards User Manual (SCUM1)*, Table 8-1. Some bioassays conducted by methods outside of SMS rule, but still within PSEP.
	data use	Data are compared to *Sediment Management Standards WAC Chapter 173-204* Table II.
	procedures	*Sediment Source Control Standards User Manual (SCUM1*), published in 6/93, describes study and investigation procedures.
	program description	*Sediment Management Standards WAC Chapter 173-204* Sections 400-420 describe all source control functions.
	regulations	*RCW 90.48* and *Sediment Management Standards WAC Chapter 173-204* are the basis for this program.
	target lists and detection limits	*Sediment Management Standards WAC Chapter 173-204* Table II. *Sediment Source Control Standards User Manual* Table 8-1.
NPDES Water	analytical methodology	Listed in *Water Quality Program Permit Writer's Manual*, published in 7/94, based on *40 CFR Part 136*.
	data qualification	Data are not required to be qualified.
	data use	Effluent, water, and sediment data are compared to *WAC Chapter 173-201 A*. *WAC Chapter 173-201 A-040* contains narrative and numeric criteria.
	field sampling	The current version of *Recommended Protocols for Measuring Selected Environmental Variables In Puget Sound*.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
NPDES Water (continued)	program description	*Water Quality Program Permit Writer's Manual*, Ecology Publication 92-109, published in 7/94.
	regulations	• *Federal Water Pollution Control Act and Amendments, Public Law 92-500* (The Clean Water Act). • *Water Pollution Control Act. Chapter 90.48 RCW*; part 260 contains state authority, function, powers, duties. • *WAC Chapter 173-220* (state NPDES regulations). • WAC Chapter 173-201A (state water quality standards and aquatic life criteria). • *Water Quality Program Permit Writer's Manual*, published in 7/94, describes how to conduct NPDES activities. Table 7-1 contains human health criteria .
	target analytes/ detection limits	See Water Quality Standards, *WAC Chapter 173-201A*, Toxic Substances Table, for target analytes and criteria levels. Detection limits are required to be below the chemical criteria and are listed in the *Water Quality Program Permit Writer's Manual*, published in 7/94.
PSAMP Fish Task	data deliverables	A data package which can be validated is prepared.
	data qualifiers	PSAMP data qualifiers are used.
	data use	Data are used to document trends. Areas of concern may be referred to the WA Department of Health.
	field sampling	The current version of *Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound.*
	procedures	*Puget Sound Ambient Monitoring Program-Fisheries Monitoring Task Implementation Plan*, published in 6/89.
	Procedures outside of PSP&G	Cytochrome P450 and FAC Fish Bile as per NOAA National Marine Fisheries methodologies. Metro procedures for percent lipids and percent solids are used.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
PSAMP Fish Task (continued)	regulations	This program is not conducted to fulfill a regulatory requirement. However, data may be compared to regulatory guidance or used to initiate action based on regulations.
	target lists/detection limits	A listing of target chemicals and detection limits is maintained by the program manager.
PSAMP Sediment Task	analytical methodology	*Puget Sound Ambient Monitoring Program - Marine Sediment Quality Implementation Plan*, published in 11/88, refers to CLP procedures. Actual current practice uses the current version of *Recommended Protocols for Measuring Selected Environmental Variables In Puget Sound*
	data deliverables	*Puget Sound Ambient Monitoring Program - Marine Sediment Quality Implementation Plan*, published in 11/88, page 21, refers to CLP procedures.
	data qualifiers	*Puget Sound Ambient Monitoring Program-Marine Sediment Quality Implementation Plan*, published in 11/88, page 32, refers to CLP procedures. PSAMP data qualifiers are also used.
	data use	Data are compared for reference only to the following standards: Sediment Management Standards Sediment Quality Standards Table I of *WAC Chapter 173-204*. When state standards are not available, *Pollutants of Concern in Puget Sound*, EPA 910/9-91-003
	field sampling	The current version of *Recommended Protocols for Measuring Selected Environmental Variables In Puget Sound.*
	procedures	*Puget Sound Ambient Monitoring Program - Marine Sediment Quality Implementation Plan*, published in 11/88. Currently undergoing revision.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
PSAMP Sediment Task (continued)	program description	*Puget Sound Ambient Monitoring Program, Monitoring Management Committee, Final Report*, published in 4/88. Currently undergoing revision.
	regulations	This program is not conducted to fulfill a regulatory requirement. However, data may be compared to regulatory guidance or used to initiate action based on regulations.
	target lists and detection limits	*Puget Sound Ambient Monitoring Program - Marine Sediment Quality Implementation Plan*, Table 7, page 29 published in 11/88 contains detection limit ranges. The target list is not currently published and is maintained by the program manager.
PSAMP Shellfish Task	data qualifiers	Data are validated and program specific qualifiers assigned. A list of these qualifiers is maintained by the program manager.
	data use	To establish baseline conditions.
	procedures	*Puget Sound Ambient Monitoring Program - Shellfish Programs Implementation Plan*, published in 2/90.
	program description	*Puget Sound Ambient Monitoring Program - Shellfish Programs Implementation Plan*, published in 2/90.
	regulations	This program is not conducted to fulfill a regulatory requirement. However, data may be compared to regulatory guidance or used to initiate action based on regulations.
	target lists/ detection limits	*Puget Sound Ambient Monitoring Program - Shellfish Programs Implementation Plan*, Chapter 4, Tables 2 and 3.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
PSAMP Marine Water Task	data qualification	*Marine Water Column Ambient Monitoring Program: Wateryear 1993 Data Report* contains microbiology qualifiers. Published in 12/94.
	data use	Data are compared to historical/background data. Data may be compared to *Quality Criteria for Water 1986* (US EPA Gold Book), published in 1986 and updated periodically.
	field sampling	The current version of *Recommended Protocols for Measuring Selected Environmental Variables In Puget Sound.*
	procedures	*Marine Water Column Ambient Monitoring Wateryear 1995 Long-Term Monitoring Implementation Plan*, published in 5/95.
	program description	*Puget Sound Ambient Monitoring Program, Monitoring Management Committee, Final Report*, published in 4/88. Currently undergoing revision.
	regulations	This program is not conducted to fulfill a regulatory requirement. However, data may be compared to regulatory guidance or used to initiate action based on regulations.
PSDDA	target lists, detection limits	*Marine Water Column Ambient Monitoring Program: Wateryear 1993 Data Report,* Table 2, page 10, lists analytical parameters and reporting limits. Published in 12/94.
	data qualifiers	Use PSDDA DAIS data qualifiers.
	data use	Used to make regulatory decisions regarding Section 404/401 of the Clean Water Act.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
PSDDA (continued)	procedures	For sampling and testing, refer to *PSDDA Evaluation Procedures Technical Appendix*, and the *Management Plan Report - Unconfined Open Water Disposal of Dredged Material, Phase II, Appendix A*.
	program description	• *Puget Sound Dredged Disposal Analysis (PSDDA) Management Plan Report, Unconfined Open-Water Disposal of Dredged Material, Phase I (Central Puget Sound)*, also referred to as *MPR*, *1988*; published in 1988. • *Puget Sound Dredged Disposal Analysis (PSDDA) Management Plan Report, Unconfined Open-Water Disposal of Dredged material, Phase II (North and South Puget Sound),* also referred to as *MPR*, *1989;* published in 1989. • *Puget Sound Dredged Disposal Analysis (PSDDA) Management Plan Technical Appendix*, also referred to as *MPTA*, *1988*; published in 1988.
	regulations and procedures	• *MPR*, 1989. Page ES-3 provides key regulatory authorities. • *Green Book Ocean Testing Manual* provides guidance for ocean testing and disposal; published in 1991. • *Marine Protection Research and Sanctuaries Act (MPRSA)*, Section 103 (Ocean Dumping Regulations), 1972. Implementation through the Green Book Ocean Testing Manual. • *Inland Testing Manual* (Draft) guidance document on Clean Water Act Section 404 regarding dredging and disposal. • Environmental monitoring is discussed in *MPTA* Exhibit I.
	target lists and detection limits	Refer to prototype SAP, *Sampling and Analysis Plan for Sediment Characterization at Pier D*, published in 9/94.

Table A-2 (continued)

PROGRAM	TOPIC	DOCUMENT[1]
Sediment Management Standards	data reporting	QA1 review per *Puget Sound Dredged Disposal Analysis Guidance Manual - Data Quality Evaluation For Proposed Dredged Material Disposal Projects*, published in 6/89.
	data use	Data are compared to Table II (Sediment Quality Standards Chemical Criteria) and Table III (Puget Sound Marine Sediment Cleanup Screening Levels and Minimum Cleanup Levels Chemical Criteria) of the Sediment Management Standards *WAC Chapter 173-204.*
	field sampling	The current version of *Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound.*
	procedures	Sediment Management Standards *WAC Chapter 173-204* Sections 500-590 describe sediment cleanup functions. *Sediment Cleanup Standards Users Manual (SCUM2),* published in 12/91, describes data use.
	program description	Sediment Management Standards *WAC Chapter 173-204* Sections 500-590.
	regulations	Sediment Management Standards *WAC Chapter 173-204*.
	target lists, detection limits	Tables I and III in the Sediment Management Standards, *WAC Chapter 173-204.*

Notes:
1. Request information on obtaining reference documents from Program Contacts identified in Appendix C.

14. APPENDIX B: STANDARDIZED PROJECT PLANNING FORM

This appendix contains a template for a standardized project planning form. This form may not meet planning requirements for projects performed under the guidance of regulatory programs, as many of these programs require a formal planning document. However, the template may be useful to facilitate project planning for projects and studies which are being performed outside of a regulatory framework. Note that it should only be used after obtaining the approval of key participants.

Puget Sound Protocols and Guidelines
Project Planning Form

NOTE: If data are to be used to support regulatory programs, a formal planning document may be required. This form should not be used to plan for regulatory based sampling and analysis.

name of project:

lead organization:

filled out by:	organization:	phone number:
filled out by:	organization:	phone number:

KEY INDIVIDUALS AT LEAST ONE INDIVIDUAL FROM EACH ORGANIZATION

name	organization and address	(area code) phone number	project responsibility

approved by:	organization:	date:

Puget Sound Protocols and Guidelines
Project Planning Form

project objectives and expected use of the data:

description of sampling (and approximate time intervals, if applicable) and analysis

approximate sampling dates:

laboratory data	validation required: **yes** **no**	if yes, validation

SAMPLE LOCATIONS

station identification	coordinates	station identification	coordinates

Coordinate System Used:

Puget Sound Protocols and Guidelines
Project Planning Form

PARAMETER AND STATION LIST

Note: Parameters may be grouped together in ***LISTS***, see next page. Should parameters be grouped together, also provide a detailed summary of number of analyses for each parameter. Include field QC samples.

PARAMETERS

station	depth and units	matrix										
total number of samples for each parameter	(not applicable)	(not applicable)										

Puget Sound Protocols and Guidelines
Project Planning Form

If a standard parameter list(s) will be used, describe here.

list #	parameters
list 1	
list 2	
list 3	
list 4	
list 5	
list 6	

Attach additional parameter information in the above format if needed.

SAMPLE COLLECTION TECHNIQUE

matrix	parameter or list #	collection technique	stations

Puget Sound Protocols and Guidelines
Project Planning Form

SAMPLING EQUIPMENT CLEANING PROCEDURE
description of field equipment cleaning procedures:

SAMPLE TREATMENT
describe any sample treatment to be conducted between collection and analysis:

Puget Sound Protocols and Guidelines
Project Planning Form

LABORATORY REQUIREMENTS

THIS SECTION SHOULD BE DERIVED IN COLLABORATION WITH THE PROJECT LABORATORY

DETECTION LIMITS AND ANALYTICAL METHODS

parameter[a]	matrix	analytical method	required detection limit and units[b]

a. Include field determinations.
b. Attach additional detection limit information if needed.

LAB QC SAMPLES

parameter	matrix	QC sample	control limits	required frequency

Puget Sound Protocols and Guidelines
Project Planning Form

DATA REPORTING

report lab data to:

hard copy yes	electronic yes no	narrative required yes	QC information yes no	data package yes no

DATA PACKAGE CONTENTS

describe data package contents:

OTHER REPORTING REQUIREMENTS

Puget Sound Protocols and Guidelines
Project Planning Form

data will be validated by:

validated data to be reported to:	due date:

DATA QUALIFICATION

identify who will qualify the data:

identify the data qualification system to be used:

end of form

15. APPENDIX C: PROGRAM SPECIFIC REQUIREMENTS

15.1 Overview

Washington state agencies administer regulatory programs, as mandated by law, that require regular collection and analysis of environmental samples. Environmental data collection for each program varies depending upon program specific objectives. The objectives for each program determine sample types (water, sediment and/or tissue), parameters to measure, analytical methods and final data evaluation approach. Chemistry data collected in support of program objectives are often compared with applicable chemical criteria to determine regulatory compliance.

Following are descriptions of some major Puget Sound programs and tables that list chemical criteria for each program. In general, program objectives require that analytical detection limits for these chemicals not exceed criteria levels. Criteria levels are referred to in the corresponding tables as "maximum detection limits."

In some cases, programs may recommend analytical detection limits when criteria levels have not been set, or that are much lower than criteria levels. These are referred to in the tables as “recommended detection limits.” In other cases, chemical criteria may be so low that they cannot be achieved by routine analytical methods. Analytical detection levels should be reduced, when possible, to these criteria levels, which are referred to in the tables as "target detection limits." When these target detection limits are unattainable, program managers may accept detection limits which are reasonably above criteria levels. In such cases, advance approval by the regulatory agency is required, either on a program wide or project specific basis.

Environmental samples are also collected and analyzed for nonregulatory programs which conduct research to determine background chemical levels or identify changes in ambient conditions. For these programs, analytical results are evaluated relative to historical data. Known and expected chemical levels drive detection limit recommendations for these programs.

15.2 Sediment Management Standards (SMS)

Adopted by the Department of Ecology in April, 1991, the Sediment Management Standards, WAC Chapter 173-204, were promulgated to establish marine, low salinity and freshwater surface sediment management standards for the State of Washington. Under the SMS, the Department of Ecology administers a program to manage source control and cleanup activities to reduce and ultimately eliminate adverse effects on biological resources and significant threats to human health from surface sediment contamination (Ecology, 1993 and Ecology, 1991).

Sediment sampling and analysis is conducted for the SMS program to determine: 1) whether and to what extent surface sediments are contaminated; 2) whether point or nonpoint source discharges have contributed or may still be contributing to such contamination; and 3) whether contaminated sediments should be remediated. Biological testing may be used along with or in place of chemical data for these purposes.

Chemical criteria have been developed for 47 chemicals or classes of chemicals in Puget Sound sediments. These numerical criteria are based on Puget Sound apparent effects threshold (AET) values (Barrick et al., 1988). The chemical concentration criteria in Table I of WAC Chapter 173-204 establish the marine sediment quality standards (SQS). The SQS are chemical criteria used for the purpose of designating sediments, as explained in WAC Chapter 173-204 Section 320. The SQS represent concentrations below which adverse biological effects are considered to be unlikely.

Criteria in Table II of the WAC establish the maximum chemical concentrations levels that may be allowed within an authorized sediment impact zone (SIZ_{max}) due to a permitted or otherwise authorized discharge, except as provided for by the marine sediment biological effects restrictions described in WAC 173-204 Section 420 (3). Criteria on Table III of the WAC are identical to that in Table II and establish the Puget Sound marine sediment cleanup screening levels (CSL) and minimum cleanup levels (MCUL) chemical criteria. Station clusters of potential concern are determined as sites having chemical concentrations at or above cleanup screening levels. These same criteria are used as minimum cleanup level concentrations, in conjunction with biological effects criteria of WAC 173-204 Section 520 (3), to evaluate cleanup alternatives. The SIZ_{max}, CSL and MCUL represent concentrations above which adverse biological effects are likely to be significant. See Table C-1 for the sediment quality standards criteria and the sediment impact zone/cleanup criteria.

Analytical detection limits for the analysis of sediment samples are recommended for this program in the document, *Sediment Sampling and Analysis Plan (SAP) Appendix* (Ecology, 1995), an appendix to the Sediment Source Control Standards User Manual, SCUM1 (Ecology, 1993) and the Sediment Cleanup Standards User Manual SCUM2 (Ecology, 1991). Note these are recommended detection limits, not program requirements. In addition, the Sediment Management Standards stipulate that "where laboratory analysis indicates a chemical is not detected in a sediment sample, the detection limit shall be reported and shall be at or below the criteria value shown in the SMS criteria Tables I-III." SMS criteria levels are, therefore, considered to be the "maximum detection limits" allowable under this program.

All sediment data collected in Washington State are evaluated using the SMS. Under the SMS rule, the numerical sediment standards for most organic chemicals are organic carbon normalized. A Technical Information Memorandum has been prepared discussing organic carbon normalization (Michelsen, 1992). Because SMS criteria for nonionizable organic compounds are normalized to TOC, direct comparison to dry weight values cannot be made. Analytical detection limits and resultant chemical concentration data for this chemical group must be TOC normalized using the percent TOC (expressed as a decimal) measured for each sediment sample. Dry weight detection limits must be adequate to meet SMS criteria levels once TOC normalized. Exceptions are addressed in the SMS triennial review paper, subject: "Sediment Management Standards Detection Limits" (Bragdon-Cook, 1995).

Sediment data which are to be entered into the SEDQUAL database must meet program QC requirements and be reviewed and validated. Data qualifier flags will be assigned based on validation results. Tables C-2 and C-3 list QC requirements and data qualification control limits.

15.2.1 Sediment Management Standards Program Contacts

Washington State Department of Ecology
Central Programs, Environmental Review and Sediment Section

Sediment Management Standards, Source Control
Sediment Policy/Source Control Unit Supervisor
Brett Betts (360) 407-6914

Source Control Investigations, sediment impact zones
Sediment Policy/Source Control staff
Brenden McFarland (360) 407-6913

Contaminated sediments and cleanup, PSDDA coordination
Sediment Management Unit Supervisor
Rachel Friedman-Thomas (360) 407-6909

Northwest Regional Office
Regional Sediment Expert
Teresa Michelsen (206) 649-7257

Southwest Regional Office
Regional Sediment Expert
Russ McMillan (360) 407-6254

15.2.2 Additional Chemicals of Concern

Sediment investigations in virtually all cases involve measurement of chemical concentrations in sediment. Analyte lists are presented in Tables C-1 and C-2. There may also be potentially toxic contaminants known or suspected to be associated with a given site for which there are no numerical criteria [i.e., "...other toxic, radioactive, biological, or deleterious substances..." WAC Chapter 173-204-320(5)]. Association of these contaminants with a site may be due to their presence in a wastewater discharge from the site or a nearby location, or because of other historical activities at the site. Examples of these chemicals are listed below. When there is reason to believe that any such potentially toxic chemicals of concern may be present at a site, they should also be measured.

Chemical of Concern	**Reason for Suspected Presence in Sediments**[1]
Ammonia	Associated with fish processing plants and aquaculture operations
Other potentially toxic metals (e.g., beryllium, nickel)	Associated with mining wastes and metal plating operations
Organotin complexes (especially tributyltin)	Used historically in antifouling paint and, therefore, potentially associated with shipyards and marinas
Pesticides, herbicides	Associated with agriculture or with agricultural chemical companies

Petroleum compounds (e.g., benzene, toluene, ethylbenzene, xylene)	Associated with refineries, fuel storage facilities, marinas, gas stations
Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/ PCDFs)	Associated with the presence of polychlorinated biphenyls and pentachlorophenol and with pulp and paper mills using chlorination
Guaiacols and resin acids	Associated with pulp and paper mills and other wood products operations
Volatile organic compounds (e.g., trichloroethene, tetrachloroethene)	Used as solvents and in chemical manufacturing operations
Radioactive substances	Associated with nuclear power plants, nuclear processing plants, medical wastes, and military installations

1. Ecology, 1995.

Table C-1

Chemical Parameters and Detection Limits
Marine Sediment Management Standards

CHEMICAL PARAMETER	RECOMMENDED DETECTION LIMIT[1, 2]	Sediment Quality Standards Criteria[3]	Sediment Impact Zone and Cleanup Criteria[3]
METALS			
	(mg/Kg dry weight)	**(mg/Kg**	**(mg/Kg dry weight)**
Arsenic	19	57	93
Cadmium	1.70	5.1	6.7
Chromium	87	260	270
Copper	130	390	390
Lead	150	450	530
Mercury	0.14	0.41	0.59
Silver	2	6.1	6.1
Zinc	137	410	960
SEMIVOLATILE ORGANICS			
	(µg/Kg dry weight)	**(mg/Kg**	**(mg/Kg carbon)[a]**
Low Molecular Weight PAH			
LPAH		370	780
Naphthalene	700	99	170
Acenaphthylene	433	66	66
Acenaphthene	167	16	57
Fluorene	180	23	79
Phenanthrene	500	100	480
Anthracene	320	220	1200
2-Methylnaphthalene	223	38	64
High Molecular Weight PAH			
HPAH		960	5300
Fluoranthene	567	160	1200
Pyrene	867	1000	1400
Benz(*a*)anthracene	433	110	270
Chrysene	467	110	460
Total	1067	230	450
Benzo(*a*)pyrene	533	99	210
Indeno(1,2,3,-*c,d*)pyrene	200	34	88
Dibenzo(*a,h*)anthracene	77	12	33
Benzo(*g,h,i*)perylene	223	31	78
Chlorinated Hydrocarbons			
1,2-Dichlorobenzene	35	2.3	2.3
1,4-Dichlorobenzene	37	3.1	9
1,2,4-Trichlorobenzene	31	0.81	1.8
Hexachlorobenzene	22	0.38	2.3
Hexachlorobutadiene	11	3.9	6.2

Table C-1 (continued)

CHEMICAL PARAMETER	RECOMMENDED DETECTION LIMIT[1, 2]	Sediment Quality Standards Criteria[3] (Maximum Detection Limit)	Sediment Impact Zone and Cleanup Criteria[3]
SEMIVOLATILE ORGANICS (continued)			
	(µg/Kg dry weight)	**(mg/Kg carbon)**	**(mg/Kg carbon)**
Phthalates			
Dimethylphthalate	24	53	53
Diethylphthalate	67	61	110
di-*n*-Butylphthalate	467	220	1700
Butylbenzylphthalate	21	4.9	64
bis(2-Ethylhexyl)phthalate	433	47	78
di-*n*-Octylphthalate	2067	58	4500
Other Semivolatile Organic Compounds			
Dibenzofuran	180	15	58
N-nitrosodiphenylamine	28	11	11
Polychlorinated Biphenyls			
Total PCBs		12	65
	(µg/Kg dry weight)	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
Ionizable Organic Compounds			
Phenol	140	420	1200
2-Methylphenol	63	63	63
4-Methylphenol	223	670	670
2,4-Dimethylphenol	29	29	29
Pentachlorophenol	120	360	690
Benzyl alcohol	57	57	73
Benzoic acid	217	650	650

Notes:
1. The Sediment Sampling and Analysis Plan Appendix to the Sediment Source Control Standards User Manual (SCUM1) and the Sediment Cleanup Standards User Manual (SCUM2).
2. Numerical Recommended Detection Limit values currently under review.
3. Marine Sediment Quality Standards Chemical Criteria, WAC Chapter 173-204, Table I.
a. Units in mg/kg carbon represent concentrations in parts per million, normalized to organic carbon. To normalize to TOC, the dry weight concentration for each parameter is divided by the decimal fraction representing the percent TOC content of the sediment.

In some cases, recommended dry weight detection limits may exceed criteria levels once normalized to TOC. In these cases, lower dry weight detection limits are needed to meet criteria levels. Ecology has determined that, provided there is justification when detection limits cannot be attained to meet chlorinated hydrocarbon criteria levels, dry weight detection limits recommended in SCUM1 are acceptable. See Triennial Review paper, Sediment Management Standards (SMS) Rule, WAC Chapter 173-204, "Sediment Management Standards Detection Limits" (Bragdon-Cook, 1995).

To determine a target "µg/Kg dry weight" detection limit for each "mg/Kg carbon" value, multiply the mg/Kg carbon value by the decimal percent TOC content of the sediment and again by 1,000. For example:

If the sediment sample TOC content is determined to be 2 percent, dry weight detection limit for 1,2-dichlorobenzene would be:

2.3 mg/Kg carbon x 0.02 x 1,000 = 46 µg/Kg maximum "µg/Kg dry weight" detection limit.

Table C-2

QC Samples Used for SEDQUAL Data Qualification[1]

PARAMETER	BLANKS	REPLICATES	TRIPLICATES	MATRIX SPIKE[2]	CRM [2]	SURROGATES
Semivolatile Organics	1 per batch	5 % minimum	required if batch size > 20, 5% minimum	5 % minimum	1 per 50 samples	all samples
Pesticides/PCBs	1 per batch	5 % minimum	required if batch size > 20, 5% minimum	5 % minimum	1 per 50 samples	all samples
Volatile Organics	1 per batch or 12 hour shift, use more frequent	5 % minimum	required if batch size > 20, 5% minimum	5 % minimum	NA	all samples
Metals	5 % minimum	5 % minimum	NA	5 % minimum	5 % minimum	NA
Conventional Parameters	5 % minimum	NA	5 % minimum	NA	1 per survey	NA
Percent Solids	NA	NA	5 % minimum	NA	NA	NA
Particle Size Distribution	NA	NA	5 % minimum	NA	NA	NA

Notes:

1. This table is based on QC samples used to apply SEDQUAL data qualifiers. QC sample frequencies are based on guidance established in the following document: *Puget Sound Dredged Disposal Analysis Guidance Manual* (Ecology, 1989). Table C-3 lists data qualifiers and control limit requirements.
2. Matrix spike required for all parameters except organics parameters if isotope dilution is used.

CRM Certified reference material.

NA Not applicable.

PCB Polychlorinated biphenyl.

Table C-3

Data Qualification Control Limits[1]
SEDQUAL Data Qualifiers

CONDITION TO QUALIFY	DATA	ORGANICS QC LIMITS	METALS QC LIMITS	CONVENTIONALS QC
contamination reported in blank	B	detected in method blank	detected in method blank	detected in method blank
high duplicate RPD	E	> 100% RPD	> 20 % RPD	> 20 % RPD
high triplicate RSD	E	> 100% RSD	> 20 % RSD	> 20 % RSD
low matrix spike recovery	G	< 50 %	< 75 %	NA
low SRM recovery	G	< 95 % confidence	< 80 %	< 95 % confidence interval[a]
biased data, based on low surrogate	G	< 50 %	NA	NA
high matrix spike recovery	L	> 150 %	> 125 %	NA
high SRM recovery	L	> 95 % confidence	> 120 %	> 95 % confidence interval[a]
biased data, based on high surrogate	L	> 150 %	NA	NA
post digestion spike outside control	W	NA	see below[b]	NA
very low matrix spike recovery	X	< 10 %	< 10 %	NA
very biased data, based on low	X	< 10 %	NA	NA

Notes:
1. QC control limits are based on guidance established in the following document: *Puget Sound Dredged Disposal Analysis Guidance Manual* (Ecology, 1989).
2. A complete listing of SEDQUAL data qualifier codes is presented in Table D-1.
a. Confidence interval refers to a supplier-provided range within which there is 95 percent certainty that the true value lies.
b. Post-digestion spike recovery for GFAA analysis not within 85 to 115 percent control limits and sample absorbance less than 50 percent of spike absorbance.
CRM Certified reference material.
NA Not applicable.
RPD Relative percent difference.
RSD Relative standard deviation.
SRM Standard reference material.

15.3 PUGET SOUND DREDGED DISPOSAL ANALYSIS (PSDDA) PROGRAM

Since 1989 the management of clean dredged material and open-water disposal in Puget Sound has been accomplished through a cooperative interagency/intergovernmental activity called the Puget Sound Dredged Disposal Analysis (PSDDA) program. The four cooperating agencies are the Corps of Engineers (Seattle District), the U.S. Environmental Protection Agency (Region 10), Washington State Department of Ecology and the Washington Department of Natural Resources. The PSDDA program was initiated through a comprehensive interagency study which identified acceptable open-water disposal sites, developed state of the art evaluation procedures to characterize the suitability of sediments for disposal at those sites, and provided objective standards for management of the sites (Kendall, et al., 1994).

Sediment sampling and analysis is conducted under the PSDDA program to determine whether the overall sediment matrix (volume) proposed for dredging, when dredged and discharged at unconfined, open water disposal sites within Puget Sound, could cause or contribute to unacceptable adverse effects on the aquatic environment. Under PSDDA, chemical analyses are always required, and may in some cases be followed by biological testing if chemical screening levels are exceeded (Ecology, 1995).

The PSDDA program has established screening levels and maximum levels for 58 chemicals or classes of chemicals in Puget Sound sediments, including additional selected chemicals of concern [butyltins (tributyltin; TBT), dioxins, guaiacols, chlorinated guaiacols, chromium, and tri-, tetra-, and pentachlorobutadienes]. The PSDDA program has no established regulatory limits for chromium, dioxin, guaiacols, chlorinated guaiacols, or tri-, tetra-, and pentachlorobutadiene and therefore uses best professional judgment on a case-by-case basis when these chemicals are required in a dredging project sediment characterization. The screening levels, as SMS criteria, are based on Puget Sound apparent effects threshold (AET) values (Table C-4), and represent concentrations below which adverse biological effects are considered to be unlikely. Maximum levels represent concentrations above which adverse biological effects are likely to be significant (Ecology, 1995).

In June 1995, the four PSDDA agencies implemented the Grays Harbor and Willapa Bay Dredged Material Management Plan. This management plan is patterned after the PSDDA management plan and generally uses the same regulatory limits established for the PSDDA program for chemicals of concern.

To meet PSDDA program objectives, analytical detection limits cannot exceed screening levels and are recommended to be much lower. Sediment data must meet program QC requirements and be reviewed and validated. Data qualifier flags will be assigned based on validation results. Tables C-5 and C-6 list QC requirements and data qualification control limits.

15.3.1 Puget Sound Dredged Disposal Analysis Program Contacts

U.S. Army Corps of Engineers, Seattle District
Dredged Material Management Office

PSDDA lead Dave Kendall	(206) 764-3768 david.r.kendall@nps.usace.army.mil
PSDDA data manager David Fox	(206) 764-6550 david.f.fox@nps.usace.army.mil
PSDDA projects Stephanie Stirling	(206) 764-6945 stephanie.k.stirling@nps.usace.army.mil

15.3.2 Additional Chemicals of Concern

The 58 chemicals listed in Table C-4 are routinely considered in the evaluation of dredged material, and are required for all surveys. Other selected chemicals may be analyzed for individual projects located near specific sources of chemicals of concern that do not exhibit a widespread distribution. Examples of additional chemicals of concern which have been identified as important in localized areas and their historic uses are listed below.

Chemical of Concern	**Reason for Suspected Presence in Sediments**[1]
Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/ PCDFs)	Associated with the presence of polychlorinated biphenyls and pentachlorophenol and with pulp and paper mills using chlorination
Coplanar polychlorinated biphenyls (PCBs)	Constituents of Aroclor® mixtures formerly used as coolants and lubricants in transformers, capacitors and other electrical equipment

1. Ecology, 1995.

Table C-4

Chemical Parameters And Detection Limits
Puget Sound Dredged Disposal Analysis Program

CHEMICAL PARAMETER	RECOMMENDED DETECTION LIMITS[1]	SCREENING LEVELS[2]
CONVENTIONALS		
	(percent)	**(percent)**
Total solids	0.1	----
Total volatile solids	0.1	----
Total organic carbon	0.1	----
Total sulfides	1	----
Ammonia	1	----
METALS		
	(mg/Kg dry weight)	**(mg/Kg dry weight)**
Antimony	2.5	20
Arsenic	2.5	57
Cadmium	0.3	0.96
Copper	15.0	81
Lead	0.5	66
Mercury	0.02	0.21
Nickel	2.5	140
Silver	0.2	1.2
Tributyltin	----	0.03
Zinc	15.0	160
VOLATILE ORGANICS		
	(µg/Kg dry weight)	**(µg/Kg dry weight)**
Trichloroethene	3.2	160
Tetrachloroethene	3.2	14
Ethylbenzene	3.2	10
Total Xylene	3.2	12
SEMIVOLATILE ORGANICS		
	(µg/Kg dry weight)	**(µg/Kg dry weight)**
Low Molecular Weight PAH		
LPAH	----	610
Naphthalene	20	210
Acenaphthylene	20	64
Acenaphthene	20	63
Fluorene	20	64
Phenanthrene	20	320
Anthracene	20	130

Table C-4 (continued)

CHEMICAL PARAMETER	RECOMMENDED DETECTION LIMITS[1]	SCREENING LEVELS[2]
SEMIVOLATILE ORGANICS		
	(µg/Kg dry weight)	**(µg/Kg dry weight)**
High Molecular Weight PAH		
HPAH	20	1800
Fluoranthene	20	630
Pyrene	20	430
Benz(*a*)anthracene	20	450
Chrysene	20	670
Total Benzofluoranthenes	20	800
Benzo(*a*)pyrene	20	680
Indeno(1,2,3,-*c,d*)pyrene	20	69
Dibenzo(*a,h*)anthracene	20	120
Benzo(*g,h,i*)perylene	20	540
Chlorinated Hydrocarbons		
1,2-Dichlorobenzene	3.2	19
1,3-Dichlorobenzene	3.2	170
1,4-Dichlorobenzene	3.2	26
1,2,4-Trichlorobenzene	6	13
Hexachlorobenzene	12	23
Phthalate Esters		
Dimethyl phthalate	20	160
Diethyl phthalate	20	97
di-*n*-Butyl phthalate	20	1400
Butyl benzyl phthalate	20	470
bis(2-Ethylhexyl)phthalate	20	3100
di-*n*-Octyl phthalate	20	6200
Phenols		
Phenol	20	120
2-Methylphenol	6	20
4-Methylphenol	20	120
2,4-Dimethylphenol	6	29
Pentachlorophenol	61	100
Miscellaneous Extractable Compounds		
Benzyl alcohol	6	25
Benzoic acid	100	400
Dibenzofuran	20	54
Dioxin	0.001[a]	
Hexachloroethane	20	1400
Hexachlorobutadiene	20	29
N-nitrosodiphenylamine	12	28

Table C-4 (continued)

CHEMICAL PARAMETER	RECOMMENDED DETECTION LIMITS[1]	SCREENING LEVELS[2]
SEMIVOLATILE ORGANICS		
	(µg/Kg dry weight)	**(µg/Kg dry weight)**
Pesticides/PCBs		
Total DDT	----	6.9
p,p'-DDE	2.3	----
p,p'-DDD	3.3	----
p,p'-DDT	6.7	----
Aldrin	1.7	10
Chlordane	1.7	10
Dieldrin	2.3	10
Heptachlor	1.7	10
Lindane	1.7	10
Total PCBs	67	130

Notes:

1. PSDDA Sediment Method Detection Limit established in SAP prototype (*Sampling and Analysis Plan for Sediment Characterization at Pier D*).

2. PSDDA Screening Level criteria are based on the 1988 Puget Sound Apparent Effect Thresholds. Detection limits should not exceed PSDDA screening levels.

a. Analysis of dioxin using EPA 1613 should strive to achieve a 2,3,7,8-tetrachloro dibenzo-*p*-dioxin detection limit less than 0.001 µg/Kg.

HPAH High molecular weight polycyclic aromatic hydrocarbons.

LPAH Low molecular weight polycyclic aromatic hydrocarbons.

PAH Polycyclic aromatic hydrocarbons.

PCB Polychlorinated biphenyl.

SAP Sampling and Analysis Plan.

Table C-5

QC Requirements for PSDDA[1]

ANALYSIS	METHOD BLANK	REPLICATES	CRM	MATRIX SPIKE	SURROGATES
Volatile Organics	1 per batch[a]	1 per batch	NA	1 per batch	all samples and QC samples
Semivolatile Organics	1 per batch	1 per batch	1 per batch	1 per batch	all samples and QC samples
Pesticides/PCBs	1 per batch	1 per batch	1 per batch	1 per batch	all samples and QC samples
Metals	1 per batch	1 per batch	1 per batch	1 per batch	NA
Ammonia	1 per batch	1 per batch	NA	NA	NA
Total Sulfides	1 per batch	1 per batch	NA	NA	NA
Total Organic Carbon	1 per batch	1 per batch	1 per batch	NA	NA
Total Solids	NA	1 per batch	NA	NA	NA
Total Volatile Solids	NA	1 per batch	NA	NA	NA
Particle Size	NA	1 per batch	NA	NA	NA

Notes:
1. QC sample types and frequencies are established in the PSDDA prototype SAP, *Sampling and Analysis Plan for Sediment Characterization at Pier D.*
a. Maximum batch size is 20 samples.
CRM Certified reference material.
NA Not applicable.
PCB Polychlorinated biphenyl.
SAP Sampling and Analysis Plan.

Table C-6

PSDDA Data Qualification Control Limits[1]

ANALYSIS	METHOD BLANK	REPLICATES	CRM	MATRIX SPIKE	SURROGATES
Volatile Organics	analyte detected	compound specific[a]	NA	compound specific[a]	compound specific[a]
Semivolatile Organics	analyte detected	compound specific[a]	not used to qualify	compound specific[a]	compound specific[a]
Pesticides/PCBs	analyte detected	compound specific[a]	not used to qualify	compound specific[a]	compound specific[a]
Metals	analyte detected	20% RPD	80% to 120%	75% to 125%	NA
Ammonia	analyte detected	20% RPD	NA	NA	NA
Total Sulfides	analyte detected	20% RPD	NA	NA	NA
Total Organic Carbon	analyte detected	20% RPD	not used to qualify	NA	NA
Total Solids	NA	20% RPD	NA	NA	NA
Total Volatile Solids	NA	20% RPD	NA	NA	NA
Particle Size	NA	NA	NA	NA	NA

Notes:
1. Updated control limits maintained on the PSDDA DAIS database. Refer questions or correspondence to Program Contacts identified in Appendix C.
a. Compound specific control limits are used. These are based on either CLP, PSDDA or previously established PSEP limits.
CRM Certified reference material.
NA Not applicable; this type of QC sample is not analyzed.
PCB Polychlorinated biphenyl.
RPD Relative percent difference.

15.4 PUGET SOUND AMBIENT MONITORING (PSAMP) PROGRAM

The Puget Sound Ambient Monitoring Program (PSAMP) was established in 1988 to provide scientifically credible information about Puget Sound, its resources and the effects of human activities over time. Together, the Puget Sound Water Quality Authority, the Department of Ecology, the Department of Fish and Wildlife, the Department of Health and the Department of Natural Resources work to monitor the sediments, water quality, biological resources (fish, shellfish, marine mammals and birds) and nearshore habitats of Puget Sound.

Objectives of PSAMP are to: 1) characterize the condition of Puget Sound in relation to its natural resources and human health, recognizing contamination problems; 2) take measurements to support specific program elements identified in the Puget Sound Water Quality Management Plan (including municipal and industrial discharge, nonpoint, shellfish, wetlands, and contaminated sediments and dredging programs); 3) provide a permanent record of significant natural and human-caused changes in key environmental indicators in Puget Sound over time; and 4) support research activities through the availability of consistent, scientifically valid data.

PSAMP has been designed to complement existing monitoring programs in the Puget Sound basin. Standardized data formats and sampling and analysis protocols enable PSAMP data to be used with data from other programs (such as SMS, PSDDA, ongoing urban bay studies and National Pollutant Discharge Elimination System compliance monitoring). The findings of PSAMP may trigger surveys to identify and investigate emerging problems (PSWQA, 1988).

Under this program, sample analysis results are evaluated against historical data and may be compared to applicable, established criteria for reference purposes. A range of analytical detection limits is recommended for chemical groups based on sample matrix, analytical instrument and method. Listings of chemical parameters and recommended detection limits for the Marine Sediment Monitoring Task (see Table C-7), Marine Water Column Task (see Table C-8), and Fish Monitoring Task (see Table C-9) follow. Table C-9 lists the maximum number of analytes that might be required; different subsets of the list may be required for different fish species. Program specific QC requirements may also be established. Tables C-10 and C-11 list example QC, calibration procedure requirements and control limit requirements for the Fish Monitoring Task.

15.4.1 Puget Sound Ambient Monitoring Program Contacts

Puget Sound Water Quality Action Team

Scott Redman (360) 407-7315

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Washington State Department of Ecology
Environmental Investigations and Laboratory Services, Ambient Monitoring Section

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Ken Dzinbal (360) 407-6672

PSAMP marine sediment monitoring
Ken Dzinbal (360) 407-6672

PSAMP marine water column monitoring
Jan Newton (360) 407-6675

PSAMP freshwater monitoring
Bill Ehinger (360) 407-6682

Washington State Department of Fish and Wildlife
Marine Resources Division, PSAMP Fish Monitoring Task

Sandra O'Neill (360) 902-2843

Washington State Department of Health
Environmental Health Programs, PSAMP Shellfish Monitoring Task

Timothy Determan (360) 586-8128

15.4.2 Additional Chemicals of Concern

The chemicals of concern have generally been found to accumulate in much higher concentrations in marine and estuarine sediments than in the water column. Variables to be monitored include selected EPA priority pollutant metals and organic compounds, as well as additional chemicals of concern. These chemicals may be recommended as determined by specific project goals, or where major sources are suspected. A list of additional chemicals of concern for the Fish Monitoring Task is presented below. Note these chemicals are not currently monitored, but may be in the future.

Chemical Contaminant	**Reason for Suspected Presence in Sediments**[1]
Tributyltin	Used historically in antifouling paint and, therefore, potentially associated with shipyards and marinas
Polychlorinated dibenzo-*p*-dioxins	Associated with the presence of polychlorinated (PCDDs) biphenyls and pentachlorophenol and with pulp and paper mills using chlorination
Coplanar polychlorinated biphenyls (PCBs)	Constituents of Aroclor® mixtures formerly used as coolants and lubricants in transformers, capacitors and other electrical equipment

1. Ecology, 1995.

Table C-7

Chemical Parameters and Detection Limits
Puget Sound Ambient Monitoring Program Marine Sediment Monitoring Task

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
METALS	
	(mg/Kg dry weight)
Priority Pollutant Metals	
Antimony	0.1 - 0.3
Arsenic	0.1
Beryllium	----
Cadmium	0.05 - 0.1
Chromium	1.0
Copper	0.1 - 0.5
Lead	0.1 - 0.5
Mercury	0.005 - 0.01
Nickel	0.1 - 0.5
Selenium	----
Silver	0.06 - 0.1
Thallium	----
Zinc	0.2
Ancillary Metals	
Aluminum	10
Barium	----
Calcium	----
Cobalt	----
Iron	0.7 - 1.0
Magnesium	----
Manganese	1.0 - 2.0
Potassium	----
Sodium	----
Vanadium	----
VOLATILE ORGANICS	
	(µg/Kg dry weight)
Halogenated Alkanes (Alkyl Halides)	
Bromodichloromethane	10-20
Bromoform	10-20
Bromomethane	10-20
Carbon tetrachloride	10-20
Chlorodibromomethane	10-20
Chloroethane (ethyl chloride)	10-20
Chloroform	10-20
Chloromethane	10-20
Dichloromethane (methylene chloride)	10-20
1,1-Dichloroethane	10-20

Table C-7 (continued)

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
VOLATILE ORGANICS (continued)	
	(µg/Kg dry weight)
Halogenated Alkanes (Alkyl Halides) (cont.)	
1,2-Dichloroethane	10-20
1,2-Dichloropropane	10-20
1,1,2,2-Tetrachloroethane	10-20
1,1,1-Trichloroethane (methyl chloroform)	10-20
1,1,2-Trichloroethane	10-20
Trichlorofluoromethane (fluorotrichloromethane)	10-20
1,1,2-Trichloro-1,2,2-trifluoroethane	10-20
Halogenated Alkenes (Alkenyl Halides)	
1,1-Dichloroethene (1,1-dichloroethylene)	10-20
cis-1,2-Dichloroethene	10-20
trans-1,2-Dichloroethene	10-20
cis-1,3-Dichloropropene	10-20
trans-1,3-Dichloropropene	10-20
Monochloroethylene (vinyl chloride)	10-20
Tetrachloroethene	10-20
Trichloroethene	10-20
Aromatic and Chlorinated Aromatic Compounds	
Benzene	10-20
Chlorobenzene	10-20
Ethylbenzene	10-20
Styrene (vinylbenzene)	10-20
Toluene	10-20
Total xylenes	10-20
Ketones	
Acetone	10-20
2-Butanone	10-20
2-Hexanone	10-20
4-Methyl-2-pentanone	10-20
Ethers	
2-Chloro-ethyl vinyl ether	10-20
Esters	
Vinyl acetate	10-20
Organosulfur Compounds	
Carbon disulfide	10-20
SEMIVOLATILE ORGANICS	
	(µg/Kg dry weight)
Phenols	
2,4-Dimethylphenol	20-100
2-Methylphenol	20-100
4-Methylphenol	20-100
Phenol	20-100

Table C-7 (continued)

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
SEMIVOLATILE ORGANICS (continued)	
	(µg/Kg dry weight)
Chlorinated and Nitro-substituted Phenols	
4-Chloro-3-methylphenol	20-100
2-Chlorophenol	20-100
2,4-Dichlorophenol	20-100
4,6-Dinitro-*o*-cresol	20-100
2,4-Dinitrophenol	20-100
2-Nitrophenol	20-100
4-Nitrophenol	20-100
Pentachlorophenol	20-100
2,4,5-Trichlorophenol	20-100
2,4,6-Trichlorophenol	20-100
Resin Acids and Guaiacols	
Abietic acid	20-100
Chlorodehydroabietic acid	20-100
Dehydroabietic acid	20-100
Dichlorodehydroabietic acid	20-100
4,5-Dichloroguaiacol (4,5-dichloro-2-methoxyphenol)	20-100
Isopimaric acid	20-100
2-Methoxyphenol (guaiacol)	20-100
Neoabietic acid	20-100
Palustric acid	20-100
Pimaric acid	20-100
Sandacopimaric acid	20-100
Tetrachloroguaiacol	20-100
3,4,5-Trichloroguaiacol	20-100
4,5,6-Trichloroguaiacol	20-100
Low Molecular Weight PAH	
Acenaphthene	20-100
Acenaphthylene	20-100
Anthracene	20-100
Cymene	20-100
Fluorene	20-100
2-Methylnaphthalene	20-100
Naphthalene	20-100
Phenanthrene	20-100
High Molecular Weight PAH	
Benzo(*a*)anthracene	20-100
Benzo(*a*)pyrene	20-100
Benzo(*b*)fluoranthene	20-100
Benzo(*b*+*k*)fluoranthene	20-100
Benzo(*g,h,i*)perylene	20-100

Table C-7 (continued)

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
SEMIVOLATILE ORGANICS (continued)	
	(µg/Kg dry weight)
High Molecular Weight PAH (continued)	
Benzo(*k*)fluoranthene	20-100
Chrysene	20-100
Dibenzo(*a,h*)anthracene	20-100
Fluoranthene	20-100
Indeno(1,2,3-*c,d*)pyrene	20-100
Perylene	20-100
Pyrene	20-100
Chlorinated Aromatic Compounds	
1,2-Dichlorobenzene	20-100
1,3-Dichlorobenzene	20-100
1,4-Dichlorobenzene	20-100
1,2,4-Trichlorobenzene	20-100
2-Chloronaphthalene	20-100
Hexachlorobenzene	20-100
Chlorinated Alkanes/Alkenes	
Hexachloroethane	20-100
Hexachlorobutadiene	20-100
Hexachlorocyclopentadiene	20-100
Pentachlorobutadiene isomers	20-100
Trichlorobutadiene isomers	20-100
Tetrachlorobutadiene isomers	20-100
Phthalate Esters	
bis(2-Ethylhexyl)phthalate	20-100
Butyl benzyl phthalate	20-100
di-*n*-Butyl phthalate	20-100
di-*n*-Octyl phthalate	20-100
Diethyl phthalate	20-100
Dimethyl phthalate	20-100
Miscellaneous Extractable Compounds	
Benzoic acid	20-100
Benzyl alcohol	20-100
beta-Coprostanol	20-100
beta-Sitosterol	20-100
Cholesterol	20-100
Dibenzofuran	20-100
Isophorone	20-100
Polychlorinated dibenzodioxins	20-100
Polychlorinated dibenzofurans	20-100

Table C-7 (continued)

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
SEMIVOLATILE ORGANICS (continued)	
	(µg/Kg dry weight)
Organonitrogen Compounds	
Caffeine	20-100
9(*H*)-carbazole	20-100
4-Chloroaniline	20-100
3,3'-Dichlorobenzidine	20-100
2,4-Dinitrotoluene	20-100
2,6-Dinitrotoluene	20-100
Diphenylnitrosamine (*N*-nitrosodiphenylamine)	20-100
2-Nitroaniline	20-100
3-Nitroaniline	20-100
4-Nitroaniline	20-100
Nitrobenzene	20-100
N-nitrosodi-*n*-propylamine	20-100
Ethers	
4-Bromophenyl-phenyl ether	20-100
4-Chlorophenyl-phenyl ether	20-100
bis(2-Chloroisopropyl) ether	20-100
Dichloroethyl ether [bis(2-chloroethyl) ether]	20-100
Chlorinated Pesticides	
Aldrin	50-100
alpha-Chlordane	50-100
alpha-Endosulfan (Endosulfan I)	50-100
alpha-HCH (alpha-hexachlorocyclohexane,	50-100
alpha-BHC, alpha benzene hexachloride)	50-100
beta-Endosulfan (Endosulfan II)	50-100
beta-HCH (beta-BCH)	50-100
delta-HCH (delta-BHC)	50-100
Dieldrin	50-100
Endosulfan sulfate	50-100
Endrin	50-100
Endrin aldehyde	50-100
Endrin ketone	50-100
gamma-Chlordane	50-100
gamma-HCH (Lindane)	50-100
Heptachlor	50-100
Heptachlor epoxide	50-100
Methoxychlor	50-100
p,p'-DDD	50-100
p,p'-DDE	50-100
p,p'-DDT	50-100
Toxaphene	50-100

Table C-7 (continued)

CHEMICAL PARAMETER	RECOMMENDED[1] DETECTION LIMITS
SEMIVOLATILE ORGANICS (continued)	
	(µg/Kg dry weight)
Polychlorinated Biphenyls	
Aroclor 1016	50-100
Aroclor 1221	50-100
Aroclor 1232	50-100
Aroclor 1242	50-100
Aroclor 1248	50-100
Aroclor 1254	50-100
Aroclor 1260	50-100

Notes:
1. PSAMP Marine Sediment Quality Implementation Plan (Striplin, 1988), currently under revision.
PAH Polycyclic aromatic hydrocarbons.

Table C-8

Environmental Parameters and Detection Limits
Puget Sound Ambient Monitoring Program
Marine Water Column Task

ENVIRONMENTAL PARAMETER	REPORTING UNIT	RECOMMENDED DETECTION LIMIT[1]
LABORATORY PARAMETERS		
Ammonium-Nitrogen	mg/L	0.01
Nitrite-Nitrogen	mg/L	0.01
Nitrate+Nitrite-Nitrogen	mg/L	0.01
Orthophosphate-Phosphorus	mg/L	0.01
Chlorophyll *a* and phaeopigment	µg/L	0.05
Fecal coliform bacteria	#/100 mL	1
Conductivity	µmhos/cm @ 25°C	1
CTD PARAMETERS		
Salinity	PSU[a]	0.01
Temperature	°C	0.1
pH	pH units	0.1
Dissolved oxygen	mg/L	0.1
Light transmission	% light	0.1

Notes:
1. Marine Water Column Ambient Monitoring Program: Wateryear 1993 Data Report (Newton et al., 1994).
a. Practical Salinity Unit; equivalent to part per thousand, or gram per liter.

Table C-9

Chemical Parameters and Detection Limits
Puget Sound Ambient Monitoring Program Fish Monitoring Task

CHEMICAL PARAMETER[1]	RECOMMENDED DETECTION LIMIT[2]
CONVENTIONALS	
Percent lipids	----
Percent solids	----
METALS	
	(mg/Kg wet weight)
Arsenic	0.02
Lead	0.03
Mercury	0.01
Copper	0.01
SEMIVOLATILE ORGANICS	
	(µg/Kg wet weight)
Chlorinated	
1,2,4-Trichlorobenzene	10 - 20
1,2-Dichlorobenzene	10 - 20
1,3-Dichlorobenzene	10 - 20
1,4-Dichlorobenzene	10 - 20
Hexachlorobenzene	10 - 20
Ethers	
4-Bromophenyl phenyl ether	10 - 20
4-Chlorophenyl phenyl ether	10 - 20
bis(2-Chloroethyl)ether	10 - 20
bis(2-Chloroisopropyl)ether	10 - 20
Low Molecular Weight PAH	
Acenaphthene	10 - 20
Acenaphthylene	10 - 20
Anthracene	10 - 20
Fluorene	10 - 20
Naphthalene	10 - 20
Phenanthrene	10 - 20
High Molecular Weight PAH	
Benzo(*a*)anthracene	10 - 20
Benzo(*a*)pyrene	10 - 20
Benzo(*b)*fluoranthene	10 - 20
Benzo(*g,h,i*)perylene	10 - 20
Benzo(*k*)fluoranthene	10 - 20
Chrysene	10 - 20
Dibenzo(*a,h*)anthracene	10 -
Fluoranthene	10 -
Indeno(1,2,3-*c,d*)pyrene	10 - 20
Pyrene	10 -

Table C-9 (continued)

CHEMICAL PARAMETER[1]	RECOMMENDED DETECTION LIMIT[2]
SEMIVOLATILE ORGANICS (continued)	**(ug/Kg wet weight)**
Phenols	
2,4,6-Trichlorophenol	10 - 20
2,4-Dichlorophenol	10 - 20
2,4-Dimethylphenol	10 - 20
2,4-Dinitrophenol	10 - 20
2-Chlorophenol	10 - 20
2-Nitrophenol	10 - 20
4,6-Dinitro-2-methyl phenol	10 - 20
4-Nitrophenol	10 - 20
4-Chloro-3-methylphenol	10 - 20
Pentachlorophenol	10 - 20
Phenol	10 - 20
Phthalate Esters	
bis(2-Ethylhexyl)phthalate	10 - 20
Butyl benzyl phthalate	10 - 20
di-*n*-Butyl phthalate	10 - 20
di-*n*-Octyl phthalate	10 - 20
Diethyl phthalate	10 - 20
Dimethyl phthalate	10 - 20
Organonitrogen Compounds	
2,4-Dinitrotoluene	10 - 20
2,6-Dinitrotoluene	10 - 20
9(*H*)-Carbazole	10 - 20
N-nitroso-di-*n*-propylamine	10 - 20
N-nitrosodiphenylamine	10 - 20
N-nitrosodimethylamine	10 - 20
Nitrobenzene	10 - 20
Other Semivolatile Organic Compounds	
bis(2-Chloroethoxy)methane	10 - 20
1,2-Diphenylhydrazine	10 - 20
2-Chloronaphthalene	10 - 20
Coprostanol	10 - 20
Hexachlorobutadiene	10 - 20
Hexachlorocyclopentadiene	10 - 20
Hexachloroethane	10 - 20
Isophorone	10 - 20
Pesticides	
4,4-DDD	0.1 - 5
4,4-DDE	0.1 - 5
4,4-DDT	0.1 - 5
Aldrin	0.1 - 5
alpha-BHC	0.1 - 5
alpha-Chlordane	0.1 - 5

Table C-9 (continued)

CHEMICAL PARAMETER[1]	RECOMMENDED DETECTION LIMIT[2]
SEMIVOLATILE ORGANICS (continued)	
Pesticides (cont.)	**(µg/Kg wet weight)**
beta-BHC	0.1 - 5
delta-BHC	0.1 - 5
Dieldrin	0.1 - 5
Endosulfan I	0.1 - 5
Endosulfan II	0.1 - 5
Endosulfan sulfate	0.1 - 5
Endrin	0.1 - 5
Endrin aldehyde	0.1 - 5
gamma-BHC (Lindane)	0.1 - 5
gamma-Chlordane	0.1 - 5
Heptachlor	0.1 - 5
Heptachlor epoxide	0.1 - 5
Methoxychlor	0.1 - 5
Toxaphene	0.1 - 5
PCBs	
Aroclor 1016	10 - 20
Aroclor 1221	10 - 20
Aroclor 1232	10 - 20
Aroclor 1242	10 - 20
Aroclor 1248	10 - 20
Aroclor 1254	10 - 20
Aroclor 1260	10 - 20
Hazardous Substances	
2,4,5-Trichlorophenol	10 - 20
2-Methylnaphthalene	10 - 20
2-Methylphenol	10 - 20
2-Nitroaniline	10 - 20
3-Nitroaniline	10 - 20
4-Chloroaniline	10 - 20
4-Methylphenol	10 - 20
4-Nitroaniline	10 - 20
Aniline	10 - 20
Benzoic acid	10 - 20
Benzyl alcohol	10 - 20
Dibenzofuran	10 - 20

Notes:

1. The entire list of chemical parameters may not be monitored for all fish species.
2. PSAMP Fisheries Monitoring Task Implementation Plan (Stern, 1989), currently under revision. Actual detection limits vary for each fish species monitored, and are often lower than the ranges shown on this table. Some detection limits may be higher.

BHC beta-Hexachlorocyclohexane.

PAH Polycyclic aromatic hydrocarbon.

PCB Polychlorinated biphenyl.

Table C-10

QC Requirements
Puget Sound Ambient Monitoring Program
Fish Monitoring Task

REQUIREMENT	ASSAY	REQUIRED FREQUENCY	PERFORMANCE CRITERIA (control limit unless otherwise stated)
Blanks	GC-MS	5% or 1 per batch	< 5 µg phthalates < 2.5 µg other compounds
	GC-ECD pesticides, PCBs	5%	no analyte > RDL
	metals	5%	no analyte > RDL
Replicate Lab Samples	GC-MS	5%	RSD 50% or PLOD
	GC-ECD pesticides, PCBs	5%	RSD < 100%
	metals	5%	< 20% RPD
Spiked blanks	Each assay type	at least 1 (@ ≤10x LLD)	> 50% control limit > 75% warning limit
Matrix Spikes and Duplicates	GC-MS	5%	> 50% recovery
	GC-ECD pesticides, PCBs	5%	> 50% recovery
	metals	10%	±25 % of nominal
Standard Reference Material	GC-MS	1 per 50 samples	within 95 percentile range
	GC-ECD pesticides, PCBs	1 per 50 samples	within 95 percentile range
	metals	1 per 50 samples	80 to 120% recovery[a]
Surrogate Recoveries	GC-MS	all samples	> 50% recovery[b]
	GC-ECD pesticides, PCBs	all samples	> 50% recovery[c]

Table C-10 (continued)

REQUIREMENT	**ASSAY**	**REQUIRED FREQUENCY**	**PERFORMANCE CRITERIA** (control limit unless otherwise stated)
Duplicate Injections	Metals by GFAA	all samples	$\pm$ 20% RPD if $\geq$ DL
Analytical Spikes	Metals by GFAA	all samples	100% $\pm$ 15% of nominal
MSA.	Metals by GFAA	as needed	$r \geq 0.995$
Interference Checks	Metals by ICP	2 per batch	$\leq$ 20% of mean response

Notes:
a. Or within acceptance limits, whichever is greater.
b. 50 percent recovery for majority of surrogates.
c. For at least 1 of the 2 surrogates.
DL Detection limit.
GC-ECD Gas chromatography - electron capture detection.
GC-MS Gas chromatography - mass spectrometry.
GFAA Graphite furnace atomic absorption detection.
ICP Inductively coupled argon plasma spectrophotometry
LLD Lower limit of detection.
MSA Method of standard addition.
PCB Polychlorinated biphenyl.
PLOD Project limit of detection.
RDL Reporting detection limit.
RPD Relative percent difference.
RSD Relative standard deviation.

Table C-11

Calibration Procedures and Control Limits
Puget Sound Ambient Monitoring Program
Fish Monitoring Task

METHOD	GC-MS	GC-ECD	GFAA; ICP-AES; ICP-MS	CVAA
Analytes	semivolatile organics	pesticides and PCBs	metals	mercury
Calibrant Requirements	EPA traceable analytes, DFTPP,	EPA traceable analytes and surrogates; ≥5	NIST - traceable	NIST - traceable
INITIAL CALIBRATION / FULL RESPONSE				
Frequency	1/ submission plus as required	1/ submission plus as required	Daily and each time instrument is set up	Daily and each time instrument is set up
Control Limits	≤ 25% RSD of RRFs for 5 levels[a]	≤ 25% RSD of RRFs for 5 levels	NOTE: For GFAA and CVAA run 1 blank and 3 standards. For ICP-AES 1 blank and 1 standard. For ICP-MS run 1 blank and 3 standards. PLUS - run a standard at the PLOD for all analytes	
CALIBRATION CHECKS				
Frequency (use most	beginning and end of shift: or 1 per 12 hours	beginning and end of shift: or 1 per 6 hours	1 per 2 hours; or 1 per 10 samples	1 per 2 hours; or 1 per 10 samples
Control Limits	RPD of RRFs ≤ 40%	RPD ≤ 25%	± 10% (MSA samples ± 20%)	± 20%

Notes:
a. The following compounds are excluded from this requirement: bis(2-ethylhexyl)phthalate; butylbenzylphthalate; carbazole; 4-chloroaniline; 3,3'-dichlorobenzidine; diethylphthalate; dimethylphthalate; di-*n*-butylphthalate; di-*n*-octylphthalate; 2,4-dinitrophenol; 4,6-dinitro-2-methyl phenol; hexachlorobutadiene; hexachlorocyclopentadiene; 2-nitroaniline; 3-nitroaniline; 4 nitroaniline; 4-nitrophenol; N-nitrosodiphenylamine; 2,4,6-tribromophenol.

CVAA Cold vapor atomic absorption spectroscopy.
DFTPP Decafluorotriphenylphosphine.
EPA United States Environmental Protection Agency.
GC-ECD Gas chromatography/electron capture detection.
GC-MS Gas chromatography/mass spectrometry.
GFAA Graphite furnace/atomic absorption spectroscopy.
ICP-AES Inductively-coupled plasma/atomic emission spectroscopy.
ICP-MS Inductively-coupled plasma/ mass spectrometry.
MSA Method of standard addition.
NIST United States National Institute of Standards and Technology.
PLOD Project limit of detection.
RPD Relative percent difference.
RRF Relative response factor.
RSD Relative standard deviation.

15.5 NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES) PROGRAM

The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) and its revisions, collectively called "The Clean Water Act," created a system for permitting municipal and industrial wastewater discharges under Section 402. To implement the goals and policies of the Act, WAC Chapter 173-220, National Pollutant Discharge Elimination System Permit Program, establishes a state individual permit program applicable to the discharge of pollutants and other wastes and materials to surface waters of the state. The Department of Ecology administers this program for the State of Washington.

NPDES permits contain effluent limits which restrict the amount of pollutants that may be discharged. The limits may be based on the technology available to treat the pollutants (technology-based) or they may be based on the effect of the pollutants in the receiving water (water quality-based) (Ecology, 1994). Permits specify average and maximum concentration and mass limitations for discharged pollutants and may authorize dilution zones (WAC Chapter 173-220). Effluent samples are analyzed at frequent intervals for compliance with specified limits. Ultimately, a discharge authorized by NPDES permit cannot violate applicable water quality standards developed to protect human health and aquatic life.

Permitted facilities may also be required to monitor receiving water and sediments. Receiving water samples are evaluated using freshwater or marine water criteria for aquatic life per WAC Chapter 173-201A, *Water Quality Standards for Surface Waters of the State of Washington* (see Table C-12) and human health criteria per 40 CFR 131 (CFR, 1992), the "National Toxics Rule" (see Table C-13). Current analytical methods may be unable to achieve detection limits at water quality criteria levels. These criteria levels are, therefore, considered "target detection limits" and are addressed on a case-by-case basis by the NPDES program.

Marine sediment samples are evaluated using criteria established in the Sediment Management Standards, WAC Chapter 173-204. Freshwater sediment criteria are currently under development. See the Sediment Management Standards Program section in this appendix for discussion of sediment sample detection limits. A comparison of chemical parameters and detection limits between the SMS, PSDDA and PSAMP programs is presented in Table C-14.

15.5.1 NPDES Program Contacts

Washington State Department of Ecology
Water Quality Program, Permit Management Section

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Jim Krull (360) 407-6460

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Table C-12

Chemical Parameters and Detection Limits
Water Quality Standards for Aquatic Life - Marine Water

CHEMICAL PARAMETER	MARINE WATER QUALITY STANDARDS (Maximum Detection Limit)[1]
	(mg/L)
Ammonia (non-ionized NH_3)	0.035
	(µg/L)
Aldrin/Dieldrin[a]	0.0019
Arsenic	36.0
Cadmium	8.0
Chlordane	0.004
Chlorine (total residual)	7.5
Chlorpyrifos	0.0056
Chromium (hexavalent)	50.0
Copper	2.5
Cyanide	1.0
DDT (and metabolites)	0.001
Dieldrin/Aldrin[a]	0.0019
Endosulfan	0.0087
Endrin	0.0023
Heptachlor	0.0036
Hexachlorocyclohexane (Lindane)	0.16
Lead	5.8
Mercury	0.025
Nickel	7.9
Pentachlorophenol (PCP)	7.9
PCBs	0.030
Selenium	71.0
Silver	1.2
Toxaphene	0.0002
Zinc	76.6

Notes:
1. *Water Quality Standards for Surface Waters of the State of Washington*, WAC Chapter 173-201A-40 (Toxic Substances, Marine Waters).
a. Aldrin is metabolically converted to dieldrin. Therefore, the sum of the aldrin and dieldrin concentrations are compared with the dieldrin criterion.
PCB Polychlorinated biphenyl.

Table C-13

Chemical Parameters and Detection Limits
NPDES Program
Human Health Criteria

CHEMICAL PARAMETERS	(Target Detection Limits)[1] HUMAN HEALTH CRITERIA[2] FOR CONSUMPTION OF: FRESH WATER & ORGANISMS	MARINE ORGANISMS
METALS		
	(µg/L)	**(µg/L)**
Antimony	14[a]	4,300[a]
Arsenic	0.018[a,b,c]	0.14[a,b,c]
Mercury	0.14	0.15
Nickel	610[a]	4,600[a]
Thallium	1.7[a]	6.3[a]
	(fibers/L)	**(fibers/L)**
Asbestos	7,000,000[d]	----
ORGANICS		
Base/Neutral/Acid Extractables	**(µg/L)**	**(µg/L)**
2,3,7,8-TCDD (Dioxin)	0.000000013[c]	0.000000014[c]
Acrolein	320	780
Acrylonitrile	0.059[a,c]	0.66[a,c]
Benzene	1.2[a,c]	71[a,c]
Bromoform	4.3[a,c]	360[a,c]
Carbon Tetrachloride	0.25[a,c]	4.4[a,c]
Chlorobenzene	680[a]	21,000[a,e]
Chlorodibromomethane	0.41[a,c]	34[a,c]
Chloroform	5.7[a,c]	470[a,c]
Cyanide	700[a]	220,000[a,e]
Dichlorobromomethane	0.27[a,c]	22[a,c]
1,2-Dichloroethane	0.38[a,c]	99[a,c]
1,1-Dichloroethylene	0.057[a,c]	3.2[a,c]
1,3-Dichloropropylene	10[a]	1,700[a]
Ethylbenzene	3,100[a]	29,000[a]
Methyl Bromide	48[a]	4,000[a]
Methylene Chloride	4.7[a,c]	1,600[a,c]
1,1,2,2-Tetrachloroethane	0.17[a,c]	11[a,c]
Tetrachloroethylene	0.8[c]	8.85[c]
Toluene	6,800[a]	200,000[a]
1,1,2-Trichloroethane	0.60[a,c]	42[a,c]
Trichloroethylene	2.7[c]	81[c]
Vinyl Chloride	2[c]	525[c]
2,4-Dichlorophenol	93[a]	790[a,e]
2-Methyl-4,6-dinitrophenol	13.4	765

Table C-13 (continued)

CHEMICAL PARAMETERS	(Target Detection Limits)[1] HUMAN HEALTH CRITERIA[2] FOR CONSUMPTION OF: FRESH WATER & ORGANISMS	MARINE ORGANISMS
ORGANICS (continued)		
Base/Neutral/Acid Extractables (continued)		
	(µg/L)	**(µg/L)**
2,4-Dinitrophenol	70 [a]	14,000 [a]
Pentachlorophenol	0.28[a,c]	8.2[a,c,e]
Phenol	2,100[a]	4,600,000[a,e]
2,4,6-Trichlorophenol	2.1[a,c]	6.5[a,c]
Anthracene	9,600[a]	110,000[a]
Benzidine	0.00012[a,c]	0.00054[a,c]
Benzo(*a*)anthracene	0.0028[c]	0.031[c]
Benzo(*a*)pyrene	0.0028[c]	0.031[c]
Benzo(*b*)fluoranthene	0.0028[c]	0.031[c]
Benzo(*k*)fluoranthene	0.0028[c]	0.031[c]
bis(2-Chloroethyl)ether	0.031[a,c]	1.4[a,c]
bis(2-Chloroisopropyl)ether	1,400[a]	170,000[a]
bis(2-Ethylhexyl) phthalate	1.8[a,c]	5.9[a,c]
Chrysene	0.0028[c]	0.031[c]
Dibenzo(*a,h*)anthracene	0.0028[c]	0.031[c]
1,2-Dichlorobenzene	2,700[a]	17,000[a]
1,3-Dichlorobenzene	400	2,600
1,4-Dichlorobenzene	400	2,600
3,3'-Dichlorobenzidine	0.04[a,c]	0.077[a,c]
Diethyl phthalate	23,000[a]	120,000[a]
Dimethyl phthalate	313,000	2,900,000
di-*n*-Butyl phthalate	2,700[a]	12,000[a]
2,4-Dinitrotoluene	0.11[c]	9.1[c]
1,2-Diphenylhydrazine	0.04[a,c]	0.54[a,c]
Fluoranthene	300[a]	370[a]
Fluorene	1,300[a]	14,000[a]
Hexachlorobenzene	0.00075[a,c]	0.00077[a,c]
Hexachlorobutadiene	0.44[a,c]	50[a,c]
Hexachlorocyclopentadiene	240[a]	17,000[a,e]
Hexachloroethane	1.9[a,c]	8.9[a,c]
Indeno(1,2,3-*c,d*)pyrene	0.0028[c]	0.031[c]
Isophorone	8.4[a,c]	600[a,c]
Nitrobenzene	17[a]	1,900[a,e]
N-nitrosodimethylamine	0.00069[a,c]	8.1[a,c]
N-nitrosodiphenylamine	5[a,c]	16[a,c]
Pyrene	960[a]	11,000[a]

Table C-13 (continued)

CHEMICAL PARAMETERS	(Target Detection Limits)[1] HUMAN HEALTH CRITERIA[2] FOR CONSUMPTION OF: FRESH WATER & ORGANISMS	MARINE ORGANISMS
	(µg/L)	(µg/L)
Pesticides		
Aldrin	0.00013[a,c]	0.00014[a,c]
alpha-BHC	0.0039[a,c]	0.013[a,c]
beta-BHC	0.014[a,c]	0.046[a,c]
gamma-BHC	0.019[c]	0.063[c]
Chlordane	0.00057[a,c]	0.00059[a,c]
4-4'-DDT	0.00059[a,c]	0.00059[a,c]
4,4'-DDE	0.00059[a,c]	0.00059[a,c]
4,4'-DDD	0.00083[a,c]	0.00084[a,c]
Dieldrin	0.00014[a,c]	0.00014[a,c]
alpha-Endosulfan	0.93[a]	2.0[a]
beta-Endosulfan	0.93[a]	2.0[a]
Endosulfan sulfate	0.93[a]	2.0[a]
Endrin	0.76[a]	0.81[a,e]
Endrin aldehyde	0.76[a]	0.81[a,e]
Heptachlor	0.00021[a,c]	0.00021[a,c]
Heptachlor epoxide	0.0001[a,c]	0.00011[a,c]
Toxaphene	0.00073[a,c]	0.00075[a,c]
PCBs		
Aroclor 1016	0.000044[a,c]	0.000045[a,c]
Aroclor 1221	0.000044[a,c]	0.000045[a,c]
Aroclor 1232	0.000044[a,c]	0.000045[a,c]
Aroclor 1242	0.000044[a,c]	0.000045[a,c]
Aroclor 1248	0.000044[a,c]	0.000045[a,c]
Aroclor 1254	0.000044[a,c]	0.000045[a,c]
Aroclor 1260	0.000044[a,c]	0.000045[a,c]

Notes:

1. Current analytical methods may be unable to achieve detection limits at water quality criteria levels. These criteria levels should be considered target detection limits and are addressed on a case-by-case basis by the NPDES permitter.

2. 40 CFR Part 131 - Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; State's Compliance, Final Rule, December 22, 1992.

a. Criteria revised to reflect current agency q_1^* (carcinogenic potency factor or slope factor) or RfD (Reference Dose), as contained in the Integrated Risk Information System (IRIS). The fish tissue bioconcentration factor (BCF) from the 1980 criteria documents was retained in all cases.

b. The criterion refers to the inorganic form only.

c. Criteria in the matrix is based on carcinogenicity (0.000001) risk. For a risk level of 0.000001, move the decimal point in the matrix value one place to the right.

d. The criterion for asbestos is the MCL (56 FR 3526, January 30, 1991).

e. No criterion for protection of human health from consumption of aquatic organisms (excluding water) was presented in the 1980 criteria document or in the 1986 Quality Criteria for Water. Nevertheless, sufficient information was presented in the 1980 document to allow calculation of a criterion, even though the results of such a calculation were not shown in the document.

BHC beta-Hexachlorocyclohexane.

PCB Polychlorinated biphenyl.

TCDD Tetrachloro dibenzo-*p*-dioxin.

Table C-14

Chemical Parameters and Detection Limits
Comparison of Sediment Programs[1]

CHEMICAL PARAMETERS	**SMS PROGRAMS** Recommended[2] Detection Limit for SQS/SIZ/CSL	**SMS PROGRAMS SQS Criteria[3]** (Maximum Detection	**SMS PROGRAMS SIZ/CSL Criteria**	**PSDDA Recommended Detection Limit[2]**	**PSDDA Maximum Detection Limit for Screening Levels**	**PSAMP Recommended Detection Limit[2]**
CONVENTIONALS				(percent)		
Total solids				0.1		
Total volatile solids				0.1		
Total organic carbon				0.1		
Total sulfides				1		
Ammonia				1		
METALS	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**	**(mg/Kg dry weight)**
Antimony	-	-	-	2.5	20	0.1 - 0.3
Arsenic	19	57	93	2.5	57	0.1
Cadmium	1.70	5.1	6.7	0.3	0.96	0.05 - 0.1
Chromium	87	260	270	-	-	1.0
Copper	130	390	390	15.0	81	0.1 - 0.5
Lead	150	450	530	0.5	66	0.1 - 0.5
Mercury	0.14	0.41	0.59	0.02	0.21	0.005 - 0.01
Nickel	-	-	-	2.5	140	0.1 - 0.5
Silver	2	6.1	6.1	0.2	1.2	0.06 - 0.1
Zinc	137	410	960	15.0	160	0.2
VOLATILE ORGANICS				**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
Trichloroethene				3.2	160	10-20
Tetrachloroethene				3.2	14	10-20
Ethylbenzene				3.2	10	10-20
Total Xylenes				3.2	12	10-20

Table C-14 (continued)

CHEMICAL PARAMETERS	SMS PROGRAMS Recommended[2] Detection Limit for SQS/SIZ/CSL	SMS PROGRAMS SQS Criteria[3] (Maximum Detection	SMS PROGRAMS SIZ/CSL Criteria	PSDDA Recommended Detection Limit[2]	PSDDA Maximum Detection Limit for Screening Levels	PSAMP Recommended Detection Limit[2]
SEMIVOLATILE ORGANICS						
	(µg/Kg dry weight)	**(mg/Kg carbon)[4]**	**(mg/Kg carbon)[4]**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
LPAHs	-	370	780	-	610	-
Naphthalene	700	99	170	20	210	20-100
Acenaphthylene	433	66	66	20	64	20-100
Acenaphthene	167	16	57	20	63	20-100
Fluorene	180	23	79	20	64	20-100
Phenanthrene	500	100	480	20	320	20-100
Anthracene	320	220	1200	20	130	20-100
2-Methylnaphthalene	233	38	64	20	67	20-100
HPAHs	-	960	5300	-	1800	-
Fluoranthene	567	160	1200	20	630	20-100
Pyrene	867	1000	1400	20	430	20-100
Benz(*a*)anthracene	433	110	270	20	450	20-100
Chrysene	467	110	460	20	670	20-100
Total Benzofluoranthenes	1067	230	450	20	800	20-100
Benzo(*a*)pyrene	533	99	210	20	680	20-100
Indeno(1,2,3,-*c*,*d*)pyrene	200	34	88	20	69	20-100
Dibenzo(*a*,*h*)anthracene	77	12	33	20	120	20-100
Benzo(*g*,*h*,*i*)perylene	223	31	78	20	540	20-100
Chlorinated Hydrocarbons						
1,2-Dichlorobenzene	35	2.3	2.3	3.2	19	20-100
1,3-Dichlorobenzene	-	-	-	3.2	170	20-100
1,4-Dichlorobenzene	37	3.1	9	3.2	26	20-100
1,2,4-Trichlorobenzene	31	0.81	1.8	6	13	20-100
Hexachlorobenzene	22	0.38	2.3	12	23	20-100
Hexachlorobutadiene	11	3.9	6.2	20	29	20-100

Table C-14 (continued)

CHEMICAL PARAMETERS	SMS PROGRAMS Recommended[2] Detection Limit for SQS/SIZ/CSL	SMS PROGRAMS SQS Criteria[3] (Maximum Detection Limit)	SMS PROGRAMS SIZ/CSL Criteria	PSDDA Recommended Detection	PSDDA Maximum Detection Limit for Screening Levels	PSAMP Recommended Detection Limit[2]
SEMIVOLATILE ORGANICS (continued)						
	(µg/Kg dry weight)	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
Phthalates						
Dimethylphthalate	24	53	53	20	160	20-100
Diethylphthalate	67	61	110	20	97	20-100
di-*n*-Butylphthalate	467	220	1700	20	1400	20-100
Butylbenzylphthalate	21	4.9	64	20	470	20-100
bis(2-Ethylhexyl)phthalate	433	47	78	20	3100	20-100
di-*n*-Octylphthalate	2067	58	4500	20	6200	20-100
Ionizable Organic Compounds						
Phenol	140	420	1200	20	120	20-100
2-Methylphenol	63	63	63	6	20	20-100
4-Methylphenol	223	670	670	20	120	20-100
2,4-Dimethylphenol	29	29	29	6	29	20-100
Pentachlorophenol	120	360	690	61	100	20-100
Benzyl alcohol	57	57	73	6	25	20-100
Benzoic acid	217	650	65	100	400	20-100
	(µg/Kg dry weight)	**(mg/Kg carbon)[4]**	**(mg/Kg carbon)[4]**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
Miscellaneous Extractable Compounds						
Dibenzofuran	180	15	58	20	54	20-100
N-nitrosodiphenylamine	28	11	11	12	28	20-100
Hexachloroethane	-	-	-	20	1400	20-100

Table C-14 (continued)

CHEMICAL PARAMETERS	SMS PROGRAMS Recommended[2] Detection Limit for SQS/SIZ/CSL	SMS PROGRAMS SQS Criteria[3] (Maximum Detection	SMS PROGRAMS SIZ/CSL Criteria	PSDDA Recommended Detection Limit[2]	PSDDA Maximum Detection Limit for Screening Levels	PSAMP Recommended Detection Limit[2]
SEMIVOLATILE ORGANICS (continued)						
	(µg/Kg dry weight)	**(mg/Kg carbon)[4]**	**(mg/Kg carbon)[4]**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**	**(µg/Kg dry weight)**
PCBs						
Total PCBs		12	65	67	130	-
Aroclor 1016	6	-	-	-	-	50-100
Aroclor 1221	6	-	-	-	-	50-100
Aroclor 1232	6	-	-	-	-	50-100
Aroclor 1242	6	-	-	-	-	50-100
Aroclor 1248	6	-	-	-	-	50-100
Aroclor 1254	6	-	-	-	-	50-100
Aroclor 1260	6	-	-	-	-	50-100
Pesticides						
Total DDT	-	-	-	-	6.9	
p,p'-DDE	-	-	-	2.3	-	50-100
p,p'-DDD	-	-	-	3.3	-	50-100
p,p'-DDT	-	-	-	6.7	-	50-100
Aldrin	-	-	-	1.7	10	50-100
Chlordane	-	-	-	1.7	10	50-100
Dieldrin	-	-	-	2.3	10	50-100
Heptachlor	-	-	-	1.7	10	50-100
Lindane	-	-	-	1.7	10	50-100

Table C-14 (continued)

Notes:

1. The following programs are compared :
   Sediment Management Standards Program
   Puget Sound Dredged Disposal Analysis Program
   Puget Sound Ambient Monitoring Program Sediment Monitoring Task

2. Recommended Detection Limits:
   SMS - The Sediment Sampling and Analysis Plan Appendix to Sediment Source Control Standards User Manual (SCUM1) and Sediment Cleanup Standards User Manual (SCUM2). Fields left blank denote Recommended Detection Limit numerical values currently under review.
   PSDDA - Puget Sound Dredged Disposal Analysis sediment detection limit established for SAP prototype (Sampling and Analysis Plan for Sediment Characterization at Pier D).
   PSAMP - Puget Sound Ambient Monitoring Program Marine Sediment Quality Implementation Plan (Striplin, 1988). Currently under revision.

3. Maximum Detection Limits:
   SMS - Marine Sediment Quality Standards Chemical Criteria (WAC Chapter 173-204 Table I), Puget Sound Marine Sediment Impact Zones Maximum Chemical Criteria (WAC Chapter 173-204 Table II), and Puget Sound Marine Sediment Cleanup Screening Levels and Maximum Cleanup levels Chemical Criteria (WAC Chapter 173-204 Table III).
   PSDDA - Screening Level (SL) criteria are based on the 1988 Puget Sound Apparent Effects Thresholds. Detection limits should not exceed PSDDA SLs.

4. Units in mg/kg carbon represent concentrations in parts per million, normalized to organic carbon. To normalize to TOC, the dry weight concentration for each parameter is divided by the decimal fraction representing the percent TOC content of the sediment.
In some cases, recommended dry weight detection limits may exceed criteria levels once normalized to TOC. In these cases, lower dry weight detection limits are needed to meet criteria levels. Ecology has determined that, provided there is justification when detection limits cannot be attained to meet chlorinated hydrocarbon criteria levels, dry weight detection limits recommended in SCUM1 are acceptable. See Triennial Review paper, Sediment Management Standards (SMS) Rule, WAC Chapter 173-204, "Sediment management Standards Detection Limits" (Bragdon-Cook, 1995).
To determine a target "µg/Kg dry weight" detection limit for each "mg/Kg carbon" value, multiply the mg/Kg carbon value by the decimal percent TOC content of the sediment and again by 1,000. For example:
   If the sediment sample TOC content is determined to be 2%, dry weight detection limit for 1,2-dichlorobenzene would be:
   2.3 mg/Kg carbon x 0.02 x 1,000 = 46 µg/Kg maximum "µg/Kg dry weight" detection limit.

SL Cleanup screening level.
HPAH High molecular weight polycyclic aromatic hydrocarbons.
LPAH Low molecular weight polycyclic aromatic hydrocarbons.
PCB Polychlorinated biphenyl.
SIZ Sediment impact zone.
SMS Sediment Management Standards.
SQS Sediment Quality Standards.

15.6 REFERENCES FOR APPENDIX C

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16. APPENDIX D: DATA QUALIFIER CODES CURRENTLY USED BY THE MAJOR PUGET SOUND ESTUARY PROGRAMS

Table D-1

Puget Sound Estuary Program Data Qualifiers

Qualifier[1]	Definition[2]
B	Analyte detected in samples and in method blank[a]
C	Combined with unresolved substances
E	Estimate
G	Value greater than minimum shown
K	Detected at less than minimum shown
L	Value less than the maximum shown
M	Value is a mean
Q	Questionable value
R	Rejected value
T	Detected below quantification limit shown
U	Undetected at the detection limit shown
X	Recovery less than 10 percent (for isotope dilution technique)
Z	Blank-corrected[b]

Notes:

1. The qualifiers in this table are not all-inclusive. Different programs may use different codes or variations of the same qualifier codes, even within the same region or program (e.g., Puget Sound Ambient Monitoring Program).

2. Data qualifiers are defined in the 1991 Puget Sound Estuary Program document *Puget Sound Estuary Program, A Project Manager's Guide to Requesting and Evaluating Chemical Analyses,* EPA 910/9-90-024.

a. The definition for the qualifier B is consistent with current usage. This data qualifier is not defined in the referenced document.

b. A qualifier is defined and listed for blank corrected data; correction of data for blank concentration is not allowed when data are used to compare to Sediment Management Standards.

Table D-2

Puget Sound Ambient Monitoring Program Fish Task Data Qualifiers

Qualifier	Definition[1]
C	Compound is reported as part of a combination of compounds
E	Quantity listed is an estimated value
G	Estimated value is greater than the minimum shown
L	Estimated value is less than the maximum shown
R	Data value rejected and not reported
U	Substance undetected at the detection limit shown
Z	Blank-corrected

Note:
1. Data qualifiers are defined in the 1991 Puget Sound Water Quality Authority document *Puget Sound Ambient Monitoring Program Data Transfer Formats Version 2*.

Table D-3

Washington State Department of Ecology SEDQUAL Data Qualifiers

Qualifier	Definition[1]
B	Analyte detected in samples and in method blank[a]
C	Combined with unresolved substances
E	Estimate
G	Estimate is greater than value shown
K	Detected at less than detection limit shown
L	Value is less than the maximum shown
M	Value is a mean
N	Estimate based on presumptive evidence
Q	Questionable value
T	Detected below quantification limit shown
U	Undetected at the detection limit shown
W	Post digestion spike outside control limits
X	Recovery less than 10 percent
Z	Blank-corrected, still above detection limit[b]

Notes:
1. Data qualifiers are defined in the 1991 Washington State Department of Ecology document, *Sediment Cleanup Standards User Manual*.
a. The definition for the qualifier B is consistent with current usage. B is defined in the referenced document as "blank-corrected down to detection limit".
b. A qualifier is defined and listed for blank corrected data; correction of data for blank concentration is not allowed when data are used to compare to Sediment Management Standards.

Table D-4

PSDDA DAIS Data Qualifiers

Qualifier	Definition[1]
B	Analyte detected in samples and in method blank
D	Diluted sample
E	Estimate
G	Estimate is greater than value shown
J	Estimate greater than SDL but less than CRDL
L	Value is less than the maximum shown
M	Doesn't meet EPA spectral criteria, but judged to be present
S	Determined through selected ion monitoring analysis
T	Chromatographic coelution
U	Undetected

Notes:
1. Data qualifiers are defined on the US Army Corps of Engineers DAIS data system. Note these qualifiers are assigned and attached by the DAIS system.
CRDL Contract required detection limit.
DAIS Dredged analysis information system.
EPA United States Environmental Protection Agency.
PSDDA Puget Sound Dredged Disposal Analysis.
SDL Sample detection limit.

Table D-5

EPA CLP Organic Data Qualifiers

Qualifier	Definition[1]
J	The analyte was positively identified, and the associated numerical value is the approximate concentration of the analyte in the sample.
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a tentative identification.
NJ	The analysis indicates the presence of an analyte that has been tentatively identified and the associated numerical value represents its approximate concentration.
R	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be analyzed.
U	The analyte was analyzed for, but was not detected above the reported sample quantitation limit.
UJ	The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.

Notes:
1. Data qualifiers are defined in the 1994 EPA Publication PB94-963501, *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. Other data qualifiers may be added by the analytical laboratory per the appropriate Statement of Work.
CLP Contract Laboratory Program.
EPA United States Environmental Protection Agency.

Table D-6

EPA CLP Inorganic Data Qualifiers

Qualifier	Definition[1]
J	The associated value is an estimated quantity.
R	The data are unusable (note: analyte may or may not be present).
U	The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.
UJ	The material was analyzed for, but was not detected. The associated value is an estimate and may be inaccurate or imprecise.

Notes:

1. These data qualifiers are defined in the 1991 EPA Publication PB94-963502, *US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (EPA, 1994c). Other data qualifiers may be added by the analytical laboratory per the appropriate Statement of Work.

CLP Contract Laboratory Program.

EPA United States Environmental Protection Agency.

17. APPENDIX E: MDL PROCEDURE PER 40 CFR PART 136

Environmental Protection Agency

APPENDIX B TO PART 136 - DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT - REVISION 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument- independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest.

Pt. 136, App. B

Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit). Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1)Obtain another sample with a lower level of analyte in the same matrix if possible.

(2)The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increased from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1}\left[\frac{\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}{n}\right]$$

$$S = (S^2)^{\frac{1}{2}}$$

where:

Xi;i=1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i=1 to n.

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha=0.99)} \quad (S)$$

where:

MDL = the method detection limit

$t_{(n-1,\ 1-\alpha=0.99)}$ = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ($_x^2$/df).

LCL = 0.64 MDL

UCL = 2.20 MDL

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B<3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12}\right]^{\frac{1}{2}}$$

if $S^2_A/S^2_B<3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

$MDL = 2.681 (S_{pooled})$

where 2.681 is equal to $t_{12, 1-\sigma = .99)}$.

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	t(n-1, .99)
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

{49 FR 43430, Oct. 26, 1984; 50 FR 694, 696, Jan. 4, 1985, as amended at 51 FR 23703, June 30, 1986}

18. APPENDIX F: EPA REGION 10 PROCEDURE FOR DETERMINATION OF DETECTION AND QUANTITATION (QUANTIFICATION) LEVELS FOR INORGANIC ANALYSES

DETERMINATION OF DETECTION AND QUANTITATION LEVELS FOR INORGANIC ANALYSES

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For: USEPA, Region 10
Under the technical direction of the Manchester Environmental Laboratory's Metals Section.
Edited by: Metals Section, USEPA
Revision No.: 1.2
Revision Date: 03/20/96

1.0 SCOPE AND APPLICATION

This procedure outlines the steps necessary to determine the instrument detection limit (IDL), the method detection limit (MDL), the reliable detection level (RDL) and the practical quantitation level (PQL) for analytical instrumentation used in analysis of inorganic samples. This method follows EPA and CLP SOW guidelines, however, the exact method is unique to the metals section of the Manchester Laboratory. This procedure does not address the considerable debate and disagreement over proper terms and methodology, rather, it is meant to provide specific directions for determining and reporting detection levels for metals analyses at this laboratory facility.

2.0 SUMMARY OF METHOD

After initial setup and calibration of the instrument, ten reagent blank samples are analyzed consecutively. The mean and standard deviation of the ten blank sample results are calculated using 9(n-1) degrees of freedom. The IDL is determined by multiplying the standard deviation by three (3σ). A low level standard (LLS) solution is made to contain concentrations of analytes at three to five times the calculated concentration of the IDL. Seven LLS samples are analyzed consecutively and according to standard analytical and quality control procedures. The standard deviation (σ with n-1) is calculated for the seven analytical results. The estimated MDL is determined by multiplying the standard deviation times three. The LLS is analyzed in the same manner on three non-consecutive days. The final MDL is the average of the three estimated MDLs. The RDL is established above the MDL to provide a practical level of detection for routine analyses. The PQL is experimentally determined by measuring analyte concentrations progressively larger than the RDL until a series of ten measurements demonstrates percent relative standard deviation of $\leq$ 10% and accuracy of the mean should be within 90 - 110% of the true value.

3.0 PROCEDURE

3.1 Initial instrument set up.

3.1.1 Set up the instrument according to the manufacturer's guidelines. Establish interference and background correction factors.

3.2 Determine the instrument detection limit (IDL).

3.2.1 Definition: The IDL is the constituent concentration that produces a signal greater than three standard deviations of the mean noise level.

3.2.2 Calibrate the instrument according to CLP and Laboratory guidelines.

3.2.3 After calibration, run initial quality control standards at CLP or Laboratory established limits as verification. Analyte concentrations should be within 90% - 110% of the known value for ICP-AES, ICP-MS; GFAAS, and FAAS analyses, 80% - 120% for CVAAS (mercury).

3.2.4 Analyze a blank solution to determine that no carryover is present in the system.

3.2.5 Prepare a high purity reagent blank solution which matches the routine sample to be analyzed by the analytical instrument.

3.2.6 Transfer the reagent blank solution to ten clean analytical containers. Treat each container as a unique, separate sample.

3.2.7 For instruments that aspirate or sparge a sample continuously:

3.2.7.1 Introduce the sample to the system and allow the aspiration or sparge to equilibrate.

3.2.7.2 Analyze a reagent blank using the same length and number of integrations and replications as is used in the routine analysis of samples.

3.2.7.3 Flush the system after each analysis according to normal operating procedures.

3.2.7.4 Repeat this procedure for the remaining reagent blanks.

3.2.8 For instruments that inject a specified volume of sample:

3.2.8.1 Inject the volume used in a routine analytical sequence.

3.2.8.2 Analyze the first reagent blank using the same length and number of integrations and replications as is used in the routine analysis of samples.

3.2.8.3 Flush the system after each analysis according to normal operating procedures.

3.2.8.4 Repeat this procedure for the remaining reagent blanks.

3.2.9 After analyzing the blank sample, run quality control standards at CLP or laboratory established limits. The criterion for acceptance is that analyte concentrations should be within 90% - 110% of the known value for ICP-AES, ICP-MS, GFAAS, and FAAS analyses, 80% - 120% for CVAAS (mercury).

3.2.10 Calculate the standard deviation (σ) by the following formula:

$$\sigma = \sqrt{\frac{\sum (v_1 - \bar{x})^2}{n-1}}$$

n = number of analyses performed (10)
v_i = the *i*th analytical value

$\bar{x}$ = average of all analytical values

3.2.11 The IDL is calculated by multiplying the standard deviation (σ) of the observed analyte concentrations by three.

$$IDL = 3 \times \sigma$$

3.3 Determine the method detection limit (MDL).

3.3.1 Definition: The MDL is the amount of constituent that produces a signal sufficiently large that 99% (3σ) of the trials with that amount will produce a detectable signal.

3.3.2 Prepare a low level standard (LLS) for the MDL determination.

3.3.2.1 The concentration of each analyte in the LLS is determined as follows.

3.3.2.1.1 Define a range for the analyte which is no less than three times the IDL but not greater than five times the IDL.

3.3.2.1.2 Define the concentration for each analyte in the LLS as a whole number within this range which can be easily manufactured by dilution of stock standards.

3.3.2.2 Prepare a stock solution which contains the analytes interest at 100-200 times the low level standard concentrations determined in the previous section.

3.3.2.3 Prepare the LLS with ultra-pure reagents matching the acid matrix of the blank solution.

3.3.2.4 Transfer the LLS solution to seven, clean, analytical containers.

3.3.3 Analyze the low level standard.

3.3.3.1 Calibrate and run initial quality control standards according to CLP and Laboratory guidelines.

3.3.3.2 Analyze a reagent blank solution just prior to analysis of the LLS to insure that no carryover contamination exists.

3.3.3.3 Analyze the LLS. Normal injection, flush time, equilibration, number of repetitions and wash-out procedures should be adhered to for the analysis.

3.3.3.4 Repeat this procedure for each of the seven LLS replicate samples.

3.3.3.5 Final quality control standards should follow the last analysis of the LLS.

3.3.3.6 Report the concentration values in the appropriate units.

3.3.3.7 Calculate an estimated MDL as follows:

$$Estimated\ MDL_{\ single\ day} = t \times \sigma$$

where, t =One-sided t distribution value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom ($t \approx 3$ for seven replicates).

σ =standard deviation of the seven replicate analyses using n-1 degrees of freedom.

3.3.3.8 Analyze the LLS according to **3.3.3** on three non-consecutive days and within a one month period.

3.3.3.9 RDLs will be determined biannually - during the months of January and June.

3.3.3.10 Calculate the final MDL by averaging the three estimated MDL determinations.

$$\text{Final MDL} = \frac{MDL_{day\ 1} + MDL_{day\ 2} + MDL_{day\ 3}}{3}$$

3.4 Establish the reliable detection level (RDL).

3.4.1 Definition: The RDL is a practical amount of constituent above the MDL which provides a reasonable level of detection to avoid false identifications of analytes at the method detection limit.

3.4.2 The RDL is established as the reportable level of detection and, as a policy decision, will be determined by the EPA Metals Team Leader.

3.4.3 The RDL is reported with two significant figures.

3.5 Determine the practical quantitation level (PQL).

3.5.1 Definition: The PQL is the experimentally determined lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions.

3.5.2 Begin by estimating the PQL at twice the RDL.

3.5.2.1 Prepare a PQL stock solution with the constituent concentrations at 100 to 200 times the estimated PQL.

3.5.2.2 Prepare the PQL working solution (analytes at the estimated PQL) with ultra-pure reagents matching the acid matrix of the blank solution.

3.5.2.3 Transfer the PQL solution to ten, clean, analytical sample containers.

3.5.3 Analyze the PQL solution.

3.5.3.1 Calibrate and run initial quality control standards according to CLP and Laboratory guidelines.

3.5.3.2 Analyze a reagent blank sample just prior to analysis of the PQL sample to insure that no carryover contamination exists.

3.5.3.3 Analyze the PQL sample. Normal injection, flush time, equilibration, number of repetitions and wash-out procedures should be adhered to for the analysis.

3.5.3.4 Repeat this procedure for each of the ten PQL replicate samples.

3.5.3.5 Final quality control standards should follow the last analysis of the PQL sample.

3.5.3.6 Report the concentration values in the appropriate units.

3.5.3.7 Calculate the mean ($\bar{x}$), standard deviation (σ) and percent relative standard deviation (%RSD) of the ten analytical results for each analyte.

$$\bar{x} = \frac{x_1 + x_2 + x_i \ldots x_{10}}{10}$$

$$\sigma = \sqrt{\frac{\sum (v_i - \bar{x})^2}{n-1}}$$

$$\%RSD = \frac{\sigma}{\bar{x}} \times 100$$

(See **3.2.10** for definitions of variables)

3.5.3.8 A valid PQL is established if the % RSD is ≤ 10% and the mean recovery of the analyte is within 90 - 110% of the true value.

3.5.3.8.1 If the limits of precision and accuracy are achieved in the first trial, the level of the PQL may have been overestimated and levels lower than twice the RDL should be evaluated. This also suggests that the RDL was overestimated and requires additional inspection.

3.5.3.9 Repeat sections **3.5.2 - 3.5.3** at three, four, five, etc. times the RDL until all analytes of interest demonstrate ≤ 10 %RSD and the mean recovery of the analyte is within 90 - 110% of the true value.

4.0 REFERENCES

Proceedings of the Fifteenth Annual EPA Conference on Analysis of Pollutants in the Environment, Office of Science and Technology, May 6-7, 1992.

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